1952

Adsorption by a cuprous oxide catalyst

Robert Carl Peabody
Iowa State University

ADSORPTION BY A CUPROUS OXIDE CATALYST

by

Robert Carl Peabody

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Inorganic Chemistry

Approved:

Signature was redacted for privacy.

In charge of Major Work

Signature was redacted for privacy.

Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College
1952

TABLE OF CONTENTS

ACKNOWLEDGMENT

The writer wishes to express his appreciation to Dr. F. E. Brown for the suggestion of the problem and for his advice and encouragement while carrying out the investigation.

INTRODUCTION

A catalyst is a substance which, by virtue of its presence, can alter the rate of a chemical reaction and which does not appear in the products of the reaction. Two general criteria are often used in determining whether a given substance is a catalyst or not. These are (a) the catalyst is found unaltered chemically at the end of the catalysis or if altered, no stoichiometric relationship exists between the amount of catalyst changed and the amounts of reactants changed, and (b) a small amount of the catalyst will bring about a relatively large amount of reaction.

Heterogeneous catalysis refers to catalytic processes in a heterogeneous system in the sense that the catalyst and the substrate are found in different phases. Heterogeneous catalysis usually involves a solid catalyst and liquid or gaseous reactants (substrates). Most catalytic hydrogenations are of the heterogeneous type.

When a solid is able to influence the rate of a reaction between gaseous reactants, it is obvious that some interaction between the solid catalyst and the gaseous reactants must occur. This interaction is called adsorption.

At least two types of adsorption are now recognized. The first of these is called van der Waal's or physical adsorption. It is characterized by a rapid, reversible adsorp-

tion of vapor which attains equilibrium rapidly. The forces responsible for this type of adsorption are the same relatively weak dipole-dipole or ion-dipole interactions which are responsible for the condensation of a gas to the liquid state. Such adsorption does not lead to dissociation of the adsorbed molecules. It occurs at relatively low temperatures and the amount of gas adsorbed decreases as the temperature is increased. Such adsorption is non-specific in nature and is not important in catalysis since it does not lead to the activation of adsorbed molecules necessary for chemical reaction.

The second type of adsorption is known as activated adsorption or chemisorption. This type of adsorption takes place at a higher temperature than the van der Waal's type, reaches equilibrium much more slowly, and has a velocity characterized by a temperature coefficient from which an apparent energy of activation can be calculated (65). Generally, both changes in temperature and pressure are necessary to reverse this type of adsorption. It is quite possible that chemisorption leads to the formation of a relatively stable surface compound which exists in stoichiometric proportions if only the surface region is considered. Whether or not compound formation is involved in chemisorption, it is certain that the adsorbed molecules on the surface of the catalyst are in an activated state conducive to

chemical reaction. The amount of material adsorbed usually increases with increasing temperature until the surface of the catalyst is saturated. It is now generally agreed that activated adsorption is a necessary part of heterogeneous catalysis.

In 1936, Menzel (48) showed that cuprous oxide is an active catalyst for the liquid phase hydrogenation of furfural to furfuryl alcohol. He also showed that the catalyst was promoted by the mechanical addition of calcium oxide. The fact that the Cu_2O-CaO mixture lacked stability lead Stewart (64) to investigate various oxides which could be added to increase the stability of the catalyst. He found that vanadium tetroxide was the best stabilizer of the oxides investigated.

The mechanism of the catalytic hydrogenation of furfural may be considered to occur in the following steps:

(1) Furfural + catalyst = adsorbed furfural

(2) H_2 + catalyst = adsorbed H_2

(3) Adsorbed furfural + adsorbed H_2 = adsorbed furfuryl alcohol

(4) Adsorbed furfuryl alcohol = furfuryl alcohol + catalyst.

In order to test the validity of this proposed mechanism, adsorption studies were started to determine the adsorptive capacity of the catalyst for the reactants and pro-

duct of the reaction.

Stanerson (63) studied the adsorptive capacity of the catalyst and its various components for hydrogen. Thus the adsorptive capacity of the catalyst for furfural and furfuryl alcohol still remained to be investigated.

HISTORICAL

Cuprous Oxide as a Catalyst

Cuprous oxide has been recognized as a catalyst for various reactions since 1923. In that year, de Loisy and Damiens (17) reported that cuprous oxide may be used as a catalyst for the conversion of ethylene to ethyl alcohol. It was shown that cuprous oxide catalyzes the formation of $C_2H_5HSO_4$ from ethylene and sulfuric acid. The ethyl hydrogen sulfate can then be hydrolyzed to ethyl alcohol.

Cuprous oxide is also a catalyst for certain decomposition reactions. In 1924, it was shown that cuprous oxide catalyzes the decomposition of hydrogen peroxide (33), and Kurtenacker and Werner (39) reported in 1927 that cuprous oxide catalyzes the decomposition of hydroxylamine in alkaline solutions.

The activity of cuprous oxide as an hydrogenation catalyst was first established by Menzel in 1936 (48).

Cuprous oxide has also been shown to be active in catalytic oxidations. The vapor phase oxidation of monoketones containing at least four carbon atoms to produce the corresponding diketones is catalyzed by cuprous oxide (52). Hearne and Adams (32) have been issued a patent for the use of cuprous oxide in the air oxidation of olefins containing at least three carbon atoms to form unsaturated aldehydes and

ketones.

Some miscellaneous uses of cuprous oxide as a catalyst include the preparation of diphenylarsenous chloride from phenylhydrazine and arsenic acid (2), the conversion of ortho or para chloronitrobenzene to the corresponding anisole or phenetole (16), and the formation of cuprene from acetylene (41).

Cuprous Oxide as an Hydrogenation Catalyst

Probably the most familiar copper catalyst for hydrogenation reactions is Adkins's copper chromite catalyst (12). The copper in this catalyst is present in the divalent state and, according to Adkins, the catalyst becomes inactive if the copper be reduced to the monovalent state (1). However, Menzel (48) has shown that cuprous oxide, promoted by the mechanical addition of calcium oxide, is an active hydrogenation catalyst. In fact, under the same conditions of temperature and pressure, this cuprous oxide catalyst is more active than Adkins's catalyst for the hydrogenation of furfural to furfuryl alcohol. Menzel also found that the method of preparation used had a profound effect on the catalytic activity of the cuprous oxide. He found that commercial samples of cuprous oxide were without activity, as were samples prepared by SO_2 reduction of cupric salts. Active cuprous oxide may be prepared by reduction of a cupric nitrate solution with glucose followed by the addition of sodium hydroxide.

Stewart (64) investigated a series of metallic oxides as promoters for Menzel's catalyst and concluded that, of the oxides investigated, vanadium tetroxide was the most effective promoter. In general, it is considered important to obtain a uniform distribution of a promoter throughout a catalyst (29). This may be accomplished by (a) co-precipitation (b) evaporation of mixed solutions or (c) moistening a powder with a solution. Thus, it is surprising that the three-component catalyst developed by Menzel and Stewart can be prepared in an active form by simply grinding the three constituents together in a mortar.

Lefrancois (40) studied the effect of varying the proportions of the three components, Cu_2O, V_2O_4 and CaO, on the activity of the catalyst in the hydrogenation of furfural and acetophenone. He came to the conclusion that the optimum proportions are Cu_2O, 1.0; V_2O_4, 0.70 and CaO, 1.4 parts by weight.

Stanerson (63) investigated the adsorption of hydrogen by the catalyst and found that adsorption occurred, starting at a temperature of 57° C. It was found that the adsorption of hydrogen was an essentially irreversible process, since only a small fraction of the adsorbed hydrogen could be removed by lowering the pressure above the catalyst. This behavior is characteristic of activated adsorption. Stanerson also found that a commercial sample of cuprous oxide did not

adsorb hydrogen even when promoted by calcium oxide. This probably explains the catalytic inactivity of such a preparation as found by Menzel. Stanerson found that there was a fair degree of correlation between adsorptive capacity for hydrogen and the catalytic activity of the various mixtures he studied.

Adsorption of Substrate and Catalytic Activity

Of the two types of adsorption now recognized, only activated adsorption is considered to be of importance in catalysis. Van der Waal's adsorption is predominately a low-temperature phenomenon and the amount of gas adsorbed by van der Waal's forces decreases as the temperature increases. Activated adsorption, on the other hand, predominates at higher temperatures. However, the two types of adsorption overlap. Activated adsorption has been demonstrated even at liquid air temperatures. Thus, a measurement of total adsorptive capacity of a catalyst includes both van der Waal's and activated adsorption. However, a correlation between adsorptive capacity and catalytic activity is to be expected only if the adsorptive capacity of the catalyst for activated adsorption is considered.

Fortunately, there are means of distinguishing between the two types of adsorption. The most delicate test for activated adsorption involves the use of isotopes. The exchange reaction $H_2 + D_2 = 2HD$ can occur only if the reacting

species are broken into atoms. If such an exchange reaction occurs on the surface of a catalyst, the adsorption which preceded the exchange reaction must have been chemisorption, since van der Waal's adsorption involves forces which are too weak to cause bond rupture. Such an exchange reaction constitutes a very delicate test for chemisorption in a temperature range where adsorption measurements alone would fail, since extensive van der Waal's adsorption may occur simultaneously. In the case of chromium oxide gel, the hydrogen exchange reaction showed that chemisorption is occurring at a temperature hundreds of degrees lower than it could be detected by adsorption measurements (28).

Another similar tool for investigating the occurrence of chemisorption involves the conversion of ortho to para hydrogen. As hydrogen naturally occurs, the ortho variety is three times as abundant as is the para variety (67). It has been found that ortho hydrogen can be converted to para hydrogen by interaction with either (a) paramagnetic molecules, ions or radicals or (b) atomic hydrogen. Thus, in the absence of paramagnetic species, the conversion of ortho to para hydrogen constitutes a sensitive test for the presence of atomic hydrogen, hence, chemisorption.

In general, however, van der Waal's adsorption is important below 0° C. If relatively large amounts of adsorption occur at higher temperatures, activated adsorption is

assumed to have occurred.

One of the most important industrial reactions involving catalysts is the synthesis of ammonia. This reaction has been subjected to careful investigation in order to determine the mechanism of the synthesis. Using a synthetic ammonia catalyst of iron, doubly promoted by Al_2O_3 and K_2O, Emmett and Brunauer have shown that the catalyst adsorbs nitrogen (Table 1, page 23) under the conditions actually prevailing during the synthesis of ammonia (21). They have also shown (22) that the rate of adsorption of nitrogen and the rate of formation of ammonia are approximately equal and thus it is probable that the rate-determining step in the synthesis of ammonia is the adsorption of nitrogen. They have also shown that the catalyst will adsorb hydrogen (10). They have succeeded recently (23) in showing that the adsorption of hydrogen and nitrogen are activated processes. It was found that the exchange reaction $N^{14}N^{14} + N^{15}N^{15} = 2N^{14}N^{15}$ occurred rapidly at 500°, at which temperature, therefore, nitrogen adsorbs and desorbs rapidly at the surface of the catalyst and synthesis of ammonia occurs. Using the hydrogen-deuterium exchange reaction, it was shown that activated adsorption of hydrogen occurs even at -195° C. Thus, the mechanism of the synthesis of ammonia on an Fe-Al_2O_3-K_2O catalyst involves the activated adsorption of both nitrogen and hydrogen.

Using the same catalyst, Taylor and Jungers (68) investigated the catalytic decomposition of ammonia into nitrogen and hydrogen. By studying the exchange reaction between NH_3 and D_2, it was established that deuterium exchanges with ammonia on an iron synthetic ammonia catalyst even at room temperature. They ascribed the exchange to the existence of adsorbed gases on the surface of the catalyst in the form of dissociated fragments, atoms in the case of D_2 and at least NH_2 and H fragments in the case of ammonia. They concluded that, even at room temperature, activated adsorption of ammonia, dissociative in nature, is freely occurring. Furthermore, since the deutero-ammonias produced (NH_2D, NHD_2 and ND_3 were all found) passed freely into the gas phase, it is evident that the reactions, $NH_3(g) = NH_2(ads) + H(ads)$; $D_2(g) = 2D(ads)$; $NH_2(ads) + D(ads) = NH_2D(g)$, and so on for more complete deuterium substitution, are all occurring freely at room temperature. Therefore, it is to be expected that such processes will occur with great rapidity at the higher temperatures (500° C.) employed in the synthesis of ammonia. Thus, such reactions cannot be expected to be rate-determining steps in such a synthesis.

The findings of Emmett and Brunauer are to be contrasted with those of Roiter, Gauchmann and Leperson (57). These authors investigated the adsorption of hydrogen and nitrogen on an iron-molybdenum catalyst, promoted by Al_2O_3, active in

the synthesis of ammonia. It was found that the catalyst chemisorbed hydrogen. At low temperatures (-184° to 0° C.) large quantities of nitrogen were adsorbed (van der Waal's adsorption). As the temperature was increased, the amount of nitrogen adsorbed decreased. At the temperatures at which ammonia synthesis began, the adsorption of nitrogen was immeasurably small. They could find no adsorption process which indicated a chemical reaction or activated adsorption. They concluded, therefore, that the adsorption of nitrogen is not involved in the synthesis of ammonia on an Fe-Mo-Al_2O_3 catalyst.

Frankenburger and Hodler (26), using a metallic tungsten catalyst active in the decomposition of ammonia to nitrogen and hydrogen, found that the catalyst not only chemisorbed ammonia, but also both nitrogen and hydrogen.

Another reaction which has received considerable study is the catalytic hydrogenation of ethylene to ethane, using various metallic catalysts, particularly copper.

In 1921, Taylor and Burns (66) found that at temperatures at which ethylene is rapidly hydrogenated (150°-200° C.) over copper, the adsorption of ethylene had become vanishingly small. Pease (53), on the other hand, found that his preparation of active copper not only adsorbed both ethylene and hydrogen, but that the adsorption of ethylene was markedly greater than that of hydrogen. The amount of ethane ad-

sorbed was quite small. On poisoning the catalyst with mercury, it was found that while the adsorption of hydrogen was reduced to one-twentieth its value on the unpoisoned catalyst, the rate of reaction was reduced to one two-hundredth its value on the unpoisoned catalyst. The adsorption of ethylene was only moderately diminished. Thus, it was evident that the catalyst must be able to adsorb both hydrogen and ethylene before it can bring about reaction.

In a further investigation, Pease (54) found the order of adsorption by copper depended on the pressure at which the comparison was made. Thus at 10 mm., the order of adsorption was: C_2H_6 greater than H_2 greater than C_2H_4; while at 760 mm., the order was: H_2 greater than C_2H_6 greater than C_2H_4; and at still higher pressures, the order was: H_2 greater than C_2H_4 greater than C_2H_6.

These observations were later confirmed by Harker (31). Still later, Turkevich and Taylor (71), while confirming the occurrence of activated adsorption of ethylene by metallic copper catalysts, showed that the picture was complicated by decomposition of the adsorbed ethylene. Thus, at 0° C., the gases desorbed by pumping analyzed 70 per cent C_2H_4 and 30 per cent C_2H_6, with some carbon being left behind on the catalyst. Apparently, the excess hydrogen used in preparing the catalyst by the reduction of CuO, and not removable by evacuation at high temperatures without sintering of the

catalyst, reacted with the adsorbed ethylene. In addition to this reaction, the adsorption was not completely reversible by desorption at 0° C. The discrepancy between the volume of ethylene adsorbed and the volume of gases desorbed increased with increasing time of contact with the catalyst. Ethane was always found in the desorbed gases even after ten successive experiments, indicating that some of the adsorbed ethylene must have undergone processes of both hydrogenation and dehydrogenation.

Ingsley (38), however, found that his preparation of a metallic copper sample, while an active catalyst for the hydrogenation of ethylene, failed to adsorb any hydrogen, ethylene or ethane. Ingsley also found that a metallic cobalt catalyst adsorbed both hydrogen and ethylene, while Taylor and Burns (66) found that such a catalyst adsorbed ethylene, but not hydrogen.

Ingsley (38) showed that an active metallic iron preparation adsorbed ethylene, but not hydrogen, while Taylor and Burns (66) found small adsorption of both ethylene and hydrogen.

Metallic nickel catalysts for the reduction of ethylene have also received considerable study. Thus, Ingsley (38) found that such a catalyst would adsorb considerable hydrogen, only a slightly smaller amount of ethylene and a small amount of ethane. This was confirmed by Taylor and Burns (66).

By use of the exchange reaction $C_2H_4 + HD = C_2H_3D + H_2$, Farkas (24) confirmed the existence of chemisorption of ethylene by metallic nickel catalysts. Since ethane did not exchange under the same conditions, it was concluded that the activated adsorption of ethane did not occur. The adsorption of ethylene was also observed by Twigg and Rideal (74).

In a recent paper, Twigg (73) discussed the results of a series of experiments in which ethylene was hydrogenated on a nickel catalyst using (a) a mixture of H_2 and D_2 and (b) the equilibrium mixture of H_2, D_2 and HD. Infra-red spectroscopic examination showed that the mixtures of ethanes produced in the two cases were identical, and were different from an equimolar mixture of C_2H_6 and $C_2H_4D_2$. This was considered to be direct proof that in the hydrogenation, the hydrogen was first dissociated into atoms on the catalyst. The mechanism proposed by Twigg to account for all the known facts in this reaction was: (1) hydrogen is not adsorbed directly on the catalyst, but only through reaction with a chemisorbed ethylene molecule to form an adsorbed ethyl radical and an adsorbed hydrogen atom; (2) hydrogenation then occurs through the addition of a hydrogen atom to the ethyl radical; (3) exchange is controlled by the reverse of the first step. A further fast reaction occurs in the union of adsorbed ethylene and a hydrogen atom to form an adsorbed

ethyl radical.

Using a platinum black catalyst for the same reaction, Maxted and Moon (44) found that both hydrogen and ethylene were chemisorbed by the catalyst. Taylor and Burns (66), however, found that their platinum catalyst would adsorb hydrogen but not ethylene.

In contrast to the behavior of most hydrogenating oxide catalysts, Cr_2O_3 is an excellent catalyst for the hydrogenation of ethylene. Gould, Bleakney and Taylor (28) have shown that Cr_2O_3 is quite active in the ortho to para hydrogen conversion, even at liquid air temperatures. Therefore, this catalyst will chemisorb hydrogen. Activated adsorption of ethylene was also demonstrated (36), although extensive decomposition of the ethylene was also found on desorption. No evidence for the activated adsorption of ethane was found. These observations were also made on a Cr_2O_3-MnO catalyst (71).

The catalytic oxidation of carbon monoxide to carbon dioxide has been the object of considerable investigation. During World War I, gas masks were developed to carry out this oxidation at room temperature. The catalyst used was hopcalite, a synthetic mixture of manganese dioxide and copper oxide. Several metals have also been found to catalyze this reaction. Metallic silver was studied by Benton and Drake (5). They found that at pressures below the

dissociation pressure of Ag_2O, activated adsorption of oxygen occurred. Benton and Bell (4) then showed that neither CO nor CO_2 was adsorbed in an activated state. They concluded that the catalytic oxidation consists of two steps (a) activated adsorption of oxygen, followed by (b) reaction of adsorbed oxygen with carbon monoxide when the latter impinges on it from the gas phase.

Hurst and Rideal (37), using a metallic copper catalyst, found that adsorption of both oxygen and carbon monoxide occurred. Since a maximum in the rate of this oxidation occurred at 175° C., at which temperature the formation of CuO from Cu and O_2 begins, they felt that the mechanism of the catalysis involved alternate oxidation and reduction of the catalyst.

Benton (3) investigated the oxides Co_2O_3, MnO-CuO, CuO, MnO_2, Fe_2O_3, V_2O_5 and SiO_2. He found that there was a direct correlation between catalytic activity of these oxides and their ability to chemisorb carbon monoxide. The same was true for the activated adsorption of both oxygen and carbon dioxide.

The chemisorption of carbon monoxide by CuO, MnO_2 and MnO-CuO catalysts was confirmed by Hoskins and Bray(35). They also found that while the adsorption of carbon monoxide was essentially reversible, a portion of the carbon monoxide was rapidly transformed to carbon dioxide.

Finkelstein, Rubanik and Khrizman (25) investigated a series of oxides including the MnO-CuO mixtures and found that while activated adsorption of oxygen occurred, no chemisorption of carbon monoxide could be found.

The combination of hydrogen and oxygen to form water is catalyzed by a number of metals. Copper, studied by Hurst and Rideal (37), was found to chemisorb both hydrogen and oxygen. Silver, investigated by Benton and Elgin (6), showed activated adsorption of oxygen, but not of hydrogen. They also investigated the adsorption of water (8), which was found to be strongly adsorbed on silver surfaces previously covered by adsorbed oxygen, which is the condition prevailing during the reaction. They concluded that the mechanism of the catalysis involves reaction on every collision of gaseous hydrogen with adsorbed oxygen, not covered by adsorbed water, in which the total energy on collision exceeds a certain value. Using a metallic gold catalyst, these same workers showed (7) that oxygen was irreversibly adsorbed in considerable quantity, but the amount of hydrogen adsorbed was immeasurably low. While kinetic measurements showed that the mechanism of the catalysis is not the same as in the case of the metallic silver catalyst, the authors proposed no mechanism to account for the observed kinetics.

The reduction of carbon monoxide by hydrogen to methane and water is catalyzed by a number of substances. Taylor and

Burns (66) found that an active metallic nickel preparation adsorbed both hydrogen and carbon monoxide. They also found that a metallic cobalt catalyst adsorbed carbon monoxide but not hydrogen. A palladium catalyst, on the other hand, adsorbed both hydrogen and carbon monoxide in large quantities. This observation was later confirmed by Taylor and McKinney (69). They also showed that the adsorption of hydrogen was complicated by diffusion into the interior of the metal.

In the Fischer-Tropsch synthesis of hydrocarbons from carbon monoxide and hydrogen, a metallic cobalt catalyst, promoted by thoria and supported on kieselguhr is used. Under certain conditions, this catalyst will selectively promote the formation of methane and water, instead of the usual oils. In studying this reaction, Craxford (15) found that extensive ortho to para hydrogen conversion occurred and so, under the conditions which result in the formation of methane, activated adsorption of hydrogen occurs. Carbon monoxide was found to be chemisorbed also under these conditions. Under the normal operating conditions which result in the formation of hydrocarbon oils, Craxford found that while the formation of a surface layer of cobalt carbide occured on the chemisorption of carbon monoxide, no ortho to para hydrogen conversion occurred. The evidence thus pointed to the first step in the Fischer-Tropsch synthesis being the reaction of chemisorbed carbon monoxide with hydrogen to give

a surface cobalt carbide and water. The next step is the reduction of this carbide by gaseous hydrogen to give higher hydrocarbons.

Certain metallic catalysts are able to hydrogenate carbon dioxide to methane and water. Taylor and Burns (66) found that while nickel catalysts chemisorbed both hydrogen and carbon dioxide, a metallic cobalt preparation adsorbed carbon dioxide but not hydrogen, and a palladium catalyst adsorbed hydrogen but no carbon dioxide. The observations concerning nickel were confirmed by Russell and Taylor (58) who used a nickel catalyst promoted by thoria.

While metallic catalysts promote the reduction of carbon monoxide to methane, oxide catalysts favor the reduction of carbon monoxide to methanol. Garner and Kingman (27), using a $ZnO-Cr_2O_3$ catalyst, demonstrated the activated adsorption of both hydrogen and carbon monoxide. Taylor and Ogden (70) studied adsorption of a $ZnO-Mo_2O_5$ catalyst and found the activated adsorption of hydrogen and of small amounts of carbon monoxide.

A number of miscellaneous catalyzed reactions have been investigated to determine which reactants are chemisorbed. Twigg (72) studied the behavior of a metallic silver catalyst active in the oxidation of ethylene to ethylene oxide and found that oxygen is chemisorbed, but not ethylene. Thus, this reaction takes place by collision of molecules of ethyl-

ene with chemisorbed oxygen.

Benzene can be hydrogenated over both platinum black and nickel. Horiuti, Ogden and Polanyi (34) investigated the activated adsorption of benzene by these catalysts at a temperature at which hydrogenation was almost imperceptible. They were able to demonstrate the exchange of deuterium for the hydrogen atoms of benzene. Either the benzene dissociates on the surface of the catalyst or else an adsorbed hydrogen atom is transferred to the adsorbed benzene while another hydrogen is detached from it. They were unable to decide which mechanism is correct.

Using an alumina catalyst active in the reaction of carbon disulfide and water to produce hydrogen sulfide, Munro and McCubbin (51) demonstrated the adsorption of carbon disulfide by the catalyst.

Crawley and Griffith (14) investigated a titanium sulfide catalyst active in the reaction $CS_2 + SO_2 = CO_2 + 3S$. It was found that activated adsorption of sulfur dioxide occurred, while on the other hand, the adsorption of carbon disulfide showed all the characteristics of the van der Waal's type.

It has been shown that the reduction of carbon disulfide by hydrogen in the presence of Ni_3S_2 leads to the formation of CH_3SH, which in turn is further reduced to hydrogen sulfide. In studying these reactions, Griffith and Hill (30)

demonstrated the activated adsorption of carbon disulfide, hydrogen and small amounts of CH_3SH. Ni_3S_2 also catalyzes the hydrogenation of sulfur dioxide to hydrogen sulfide and water. Here too, both reactants (H_2 and SO_2) were found to be chemisorbed.

Again using an Ni_3S_2 catalyst active in the reduction of COS to H_2S, Crawley and Griffith (14) found that while activated adsorption of hydrogen occurred, no adsorption of COS could be demonstrated.

In summary, it may be said that a study of the activated adsorption of the substrates by catalysts can lead to an elucidation of the mechanism of the catalysis in favorable cases. While a number of authors have found no correlation between adsorptive capacity and catalytic activity, these authors have not been careful to distinguish between activated adsorption and van der Waal's adsorption. Instead, they have been content to simply measure total adsorptive capacities. In those cases in which the distinction between the two types of adsorption has been heeded, such a correlation has often been found. In reviewing those instances in which adsorption of substrates has been studied, it becomes apparent that the activated adsorption of all the reactants is not a necessary condition for reaction; instead, in many cases, the activated adsorption of only one of the reactants is necessary.

TABLE 1

Adsorption of Substrate in Catalysis

Catalyst	Reaction	Activated adsorp.of	No Activated adsorp. of	Ref.
$Fe-Al_2O_3-K_2O$	$N_2 + 3H_2 = 2NH_3$	N_2		21
"	"	N_2		22
"	"	N_2, H_2		10
"	"	N_2, H_2		23
"	$2NH_3 = N_2 + 3H_2$	NH_3		68
$Fe-Mo-Al_2O_3$	$N_2 + 3H_2 = 2NH_3$	H_2	N_2	57
W	$2NH_3 = N_2 + 3H_2$	NH_3, H_2, N_2		26
Cu	$C_2H_4 + H_2 = C_2H_6$		C_2H_4	66
"	"	H_2, C_2H_4	C_2H_6(?)	53
"	"	C_2H_4, H_2, C_2H_6		54
"	"	H_2, C_2H_4		31
"	"	C_2H_4		71
"	"		H_2,C_2H_4,C_2H_6	38
Co	"	H_2, C_2H_4	C_2H_6(?)	
"	"	C_2H_4	H_2	66
Fe	"	C_2H_4	H_2	38
"	"	H_2, C_2H_4		66
Ni	"	H_2, C_2H_4, C_2H_6(?)		38
"	"	H_2, C_2H_4		66
"	"	C_2H_4	C_2H_6	24
"	"	C_2H_4		74

TABLE 1 (Continued)

Catalyst	Reaction	Activated adsorp. of	No Activated adsorp. of	Ref.
Ni	$C_2H_4 + H_2 = C_2H_6$	C_2H_4		73
Pt	"	H_2, C_2H_4		44
"	"	H_2	C_2H_4	66
Cr_2O_3	"	H_2, C_2H_4	C_2H_6	36
$MnO-Cr_2O_3$	"	H_2, C_2H_4		71
Ag	$2CO + O_2 = 2CO_2$	O_2		5
"	"		CO, CO_2	4
Cu	"	CO, O_2		37
Co_2O_3	"	CO, O_2, CO_2		3
MnO_2-CuO	"	CO, O_2, CO_2		3
CuO	"	CO, O_2, CO_2		3
MnO_2	"	CO, O_2, CO_2		3
Fe_2O_3	"	CO, O_2, CO_2		3
V_2O_5	"	CO, O_2, CO_2		3
SiO_2	"	CO, O_2, CO_2		3
CuO	"	CO, O_2(?), CO_2(?)		35
MnO_2	"	CO, O_2(?), CO_2(?)		35
MnO_2-CuO	"	CO, O_2(?), CO_2(?)		35
Cr_2O_3	"	O_2	CO	25
ZnO	"	O_2	CO	25
Al_2O_3	"	O_2	CO	25
Fe_2O_3	"	O_2	CO	25
MnO_2-CuO	"	O_2	CO	25

TABLE 1 (Continued)

Catalyst	Reaction	Activated adsorp. of	No Activated adsorp. of	Ref.
Cu	$2H_2 + O_2 = 2H_2O$	H_2, O_2		37
Ag	"	O_2	H_2	6
Ag	"	H_2O		8
Au	"	O_2	H_2	7
Ni	$CO + 3H_2 = CH_4 + H_2O$	CO, H_2		66
Co	"	CO	H_2	66
Pd	"	CO, H_2		66
Pd	"	CO, H_2		69
Co-ThO_2	"	CO, H_2		15
Co-ThO_2	$CO + H_2$ = oils	CO	H_2	15
Ni	$CO_2 + 4H_2 = CH_4 + 2H_2O$	CO_2, H_2		66
Co	"	CO_2	H_2	66
Pd	"	H_2	CO_2	66
Ni-ThO_2	"	CO_2, H_2		58
ZnO-Cr_2O_3	$CO + 2H_2 = CH_3OH$	CO, H_2		27
ZnO-Mo_2O_5	"	CO, H_2		70
Ag	$2C_2H_4 + O_2 = 2C_2H_4O$	O_2	C_2H_4	72
Pt	$C_6H_6 + 3H_2 = C_6H_{12}$	C_6H_6		34
Ni	"	C_6H_6		34
Al_2O_3	$CS_2 + H_2O = H_2S + ?$	CS_2		51
TiS_2	$CS_2 + SO_2 = CO_2 + 3S$	SO_2	CS_2	13
Ni_3S_2	$CS_2 + H_2 = CH_3SH + ?$	CS_2, H_2, CH_3SH		30
Ni_3S_2	$SO_2 + 3H_2 = H_2S + 2H_2O$	SO_2, H_2		30
Ni_3S_2	$COS + H_2 = H_2S + ?$	H_2	COS	14

EXPERIMENTAL

Menzel (48) determined the optimum conditions for the preparation of active cuprous oxide and found that calcium oxide was the best promoter for cuprous oxide among the following compounds: CaO, $Ba(OH)_2$, $Ca(OH)_2$, MgO, BaO, and $Ba(OH)_2 \cdot 8H_2O$.

Stewart (64) found that catalysts consisting of $Al_2O_3 \cdot xH_2O$, $Cr_2O_3 \cdot xH_2O$, $Mn(OH)_2$ and $Co(OH)_2$ coprecipitated with Cu_2O were inferior catalysts compared to Menzel's catalyst of mechanically mixed Cu_2O and CaO. Stewart also found that the mechanical addition of the following oxides also reduced the activity of Menzel's catalyst: Al_2O_3, ZnO, SnO, CoO and Mo_2O_5. However, he found that the mechanical addition of V_2O_4 or Cr_2O_3 enhanced the activity of the Cu_2O-CaO mixture.

Lefrancois (40) found that increasing the amount of V_2O_4 in the catalyst Cu_2O-V_2O_4-CaO up to a weight ratio of Cu_2O to V_2O_4 of 10 to 5 resulted in increased activity of the mixture. Increasing the amount of CaO in the catalyst up to a weight ratio of Cu_2O to CaO of 10 to 14 increased the activity of the mixture. The most active mixture contained 1.0 g. Cu_2O, 0.70 g. V_2O_4 and 1.4 g. CaO. Only this latter combination was chosen for study in the present investigation.

Preparation of Catalysts

The catalysts were prepared according to the directions

given by Stanerson (63).

Cu_2O: One thousand and eighty-five grams each of $Cu(NO_3)_2 \cdot 3H_2O$ and dextrose were dissolved in 5425 ml. of water. To this mixture was added 1736 ml. of 40 per cent NaOH solution. The precipitate was digested at 65-70° C. for 45 minutes and then filtered with suction. After washing with distilled water until the precipitate peptized and began passing through the filter paper, the precipitate was dried in a vacuum desiccator over Anhydrone. The yield was 328.4 g. of Cu_2O or 102 per cent of the theoretical. A yield greater than 100 per cent is indicative of an impure preparation.

V_2O_4: Three hundred grams of V_2O_5 was added to a solution containing 300 g. of dextrose in 1500 ml. of water and the mixture was digested on a hot plate for 24 hours. The mixture was then filtered with suction and the precipitate was washed with hot water until it peptized. The precipitate was then dried at 110° C. over night. The resulting hard blue lumps were powdered in a mortar to pass a 40 mesh sieve and then dried in a vacuum desiccator over Anhydrone. The yield was 289.5 g. of V_2O_4 or 106 per cent of the theoretical. Again, a yield greater than 100 per cent is indicative of an impure preparation.

CaO: Five pounds of reagent grade calcium oxide was ignited in a muffle furnace at 900° C. for one hour and then placed in a screw-capped bottle while still very hot. After the

solid had cooled to room temperature, the cap on the bottle was opened to the air long enough to regain atmospheric pressure. Thereafter, the bottle was kept tightly sealed when not in use.

Determination of Catalytic Activity

To determine the catalytic activity of the catalyst preparations, an hydrogenation of furfural was carried out following the procedure given by Lefrancois (40, p. 45). The reaction was carried out in a Parr Hydrogenation bomb, model B-3B. The bomb was cleaned out with soap and water, rinsed with distilled water and then acetone, and allowed to stand until dry. Seventy ml. of furfural was distilled at atmospheric pressure, the first 10-11 ml. was discarded, and the next 42 ml. (1 mole) was collected and placed in the bomb. The catalyst was prepared from 0.70 g. Cu_2O, 0.70 g. V_2O_4 and 0.525 g. CaO. These amounts were placed in a mortar and ground as rapidly as possible until homogeneous and then placed in the bomb. The bomb was sealed and placed in the shaker. Four hundred p. s. i. of tank hydrogen was added and then released to displace air from the bomb. Then 1030 p. s. i. of hydrogen was added and the bomb was rocked until the pressure became constant, at 1000 p. s. i. The time, temperature and pressure were read and the shaker and heater started. Readings of both temperature and pressure were taken every five minutes. When the temperature reached

200° C., the heater was disconnected and the bomb was rocked until the temperature reached 150° C. The results are shown in Figure 1, where a curve taken from Lefrancois's thesis, (40, p. 51), is also given.

A comparison of the two curves shows that, while in Lefrancois's case, the hydrogenation was well under way after 15 minutes, in the present case, reaction apparently began after 25 minutes of heating and shaking. The temperature of the bomb at this point was 115° C. Once the reaction began, however, it proceeded faster in the present case than in Lefrancois's case, as shown by the slopes of the straight portions of the curves in Figure 1. In the present case, this slope gives a rate of reaction of 32 p. s. i./ min., while in Lefrancois's case, the rate of reaction was 14 p. s. i./ min. The highest temperature reached by the bomb in the present case was 214° C. which occurred 45 minutes after readings were begun. Although there appears to be a longer induction period before the start of hydrogenation in the present case than in Lefrancois's case, there can be no doubt that the preparation used was catalytically active.

Analysis of Catalyst Preparations

Analysis of cuprous oxide preparation

Lefrancois (40, p. 39) reported that a sample of cuprous oxide, prepared by dextrose reduction of $Cu(NO_3)_2 \cdot 3H_2O$,

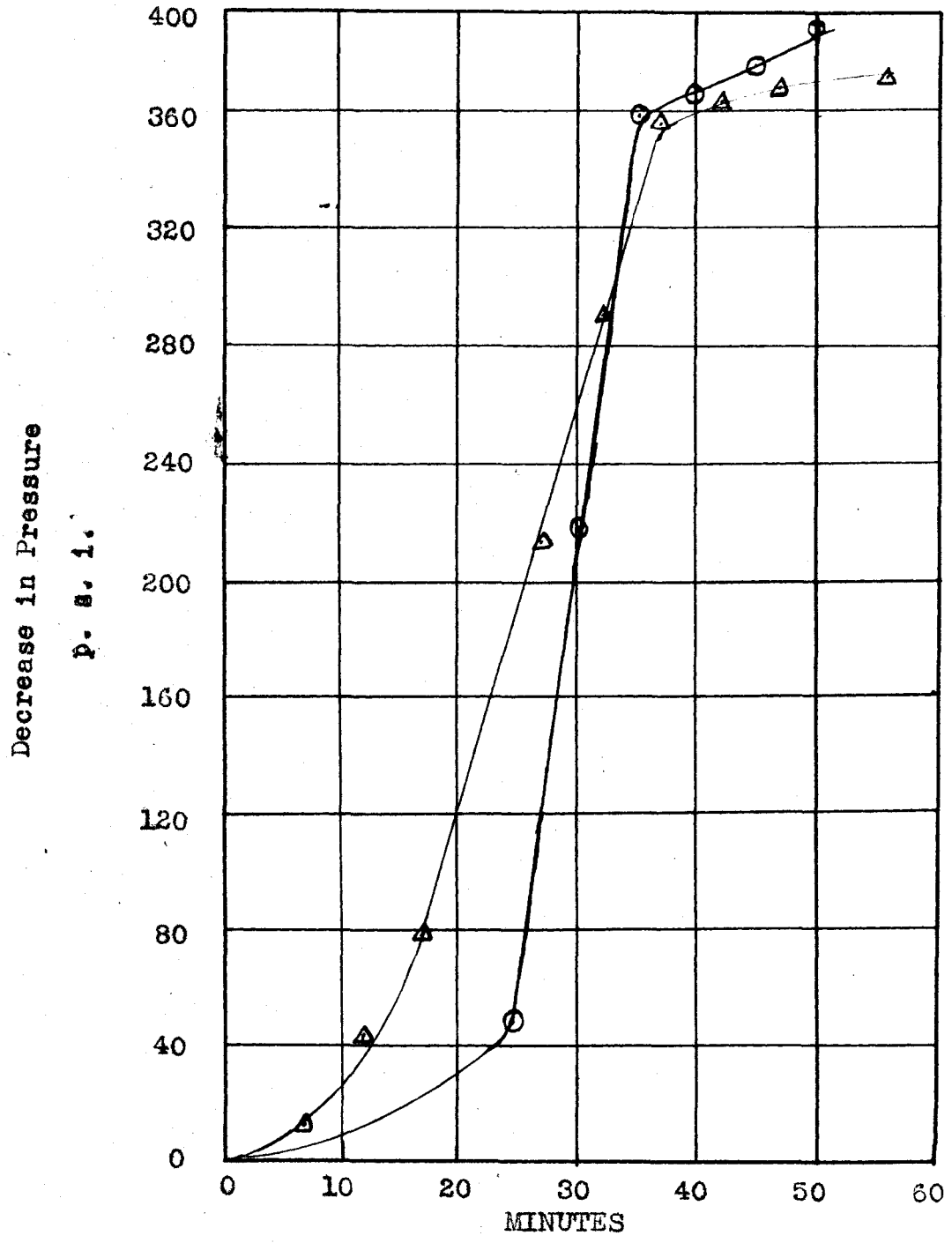


Fig. 1. Determination of Catalytic Activity
Key: △ Lefrancois's Data
⊙ Data presented on pg. 29

analyzed: $Cu = 2.12\%$

$Cu_2O = 94.12\%$

$H_2O = 3.76\%$.

The method of analysis used by Lefrancois consisted in heating a sample of the cuprous oxide preparation in an atmosphere of pure dry nitrogen. The water thus produced was collected and weighed. Next, the remaining material was reduced to copper with pure hydrogen to obtain the total per cent of copper. From this, the per cent of oxygen was calculated as the difference between 100 per cent and the sum of the per cent water and the per cent copper. The per cent cuprous oxide was then calculated, assuming all the oxygen was present as cuprous oxide. Knowing the total copper present and the copper present as cuprous oxide, the per cent metallic copper was calculated.

However, the method of analysis used by Lefrancois is incapable of distinguishing between Cu_2O and CuO. Therefore a method of analysis was sought by which one could determine not only the per cent cuprous oxide, but also the per cent metallic copper and the per cent cupric oxide.

The first method of analysis tried was the "silver sulfate-sulfuric" method of Fitzpatrick (59). This method consists in treating a sample of the cuprous oxide preparation with a neutral, saturated solution of silver sulfate, which causes the metallic copper in the sample to dissolve by displacement

of silver. The mixture is then filtered and the copper in the filtrate is determined electrolytically following the removal of silver ions in the filtrate by the addition of hydrochloric acid.

The residue of Cu_2O and CuO is transferred to a beaker and boiled with dilute sulfuric acid which brings into solution all of the copper combined as CuO and half of the copper combined as Cu_2O. The mixture is then filtered and the copper in the filtrate is determined electrolytically.

The copper in the residue, precipitated by the reaction: $Cu_2O + H_2SO_4 = Cu + CuSO_4 + H_2O$, is dissolved in hot, dilute nitric acid and determined electrolytically. This copper, expressed in terms of per cent content in the sample, multiplied by 2, gives the copper combined as Cu_2O and multiplied by 1.1258 gives the per cent Cu_2O in the sample. From the per cent of copper in the sample dissolved by dilute sulfuric acid is subtracted that precipitated by the same reaction to obtain by difference the copper combined as CuO. This multiplied by 1.2517 gives the per cent CuO in the sample.

However, the method was found to give inconsistent results. In the table below are presented some typical results given by this method of analysis.

	%Cu	%Cu_2O	%CuO
Sample I	40.82	22.89	37.30
Sample II	42.99	0.71	59.58

On the other hand, the method of Ubaldini and Guerrieri (75) seems to be satisfactory. This method consists in first determining the total copper content of the cuprous oxide preparation by treating a weighed sample (0.5 g.) with 10 ml. H_2O, 3 ml. conc. H_2SO_4 and 2 ml. conc. HNO_3, in that order. After the sample has dissolved, 65 ml. of H_2O is added and the copper determined electrolytically in the usual manner (77).

Next, the metallic copper content of the preparation is determined. A two gram sample is weighed out, wrapped in filter paper and then placed in a Soxhlet extraction thimble. The thimble is then soaked in 200 ml. of a 5 per cent solution of sulfur in CS_2 for three hours. At the end of this time, the thimble is placed in a Soxhlet extractor and washed several times with CS_2. The thimble and its contents are then dried in a vacuum desiccator. When dry, the oxides of copper are dissolved by immersing the thimble in a 200 ml. solution 8 per cent in HCl and 10 per cent in KCl.

After about an hour, the mixture is filtered and the residue washed first with the HCl-KCl mixture and then with water made slightly acidic with HCl. The sulfide remaining on the filter is dissolved in hot dilute nitric acid and the filtrate is transferred to a tall-form beaker. Three ml. of conc. H_2SO_4 is added to the filtrate and the mixture is then evaporated on a hot plate until the watch glass covering the beaker is dry. The residue is then taken up in 75 ml. H_2O,

1 ml. conc. HNO_3 is added and then 1 drop of 0.1 N HCl solution (77). The copper in the resulting solution is then determined electrolytically. The weight of copper deposited gives directly the metallic copper content of the sample.

Finally the metallic copper plus cuprous oxide content is determined. A 0.2 g. sample is dissolved in 25 ml. of a $FeCl_3$ solution prepared from 75 g. $FeCl_3 \cdot 6H_2O$, 150 ml. conc. HCl and 400 ml. H_2O. Normally, the sample dissolves rapidly. The ferrous chloride thus formed is titrated with standard N/10 ceric sulfate, using 2-3 drops of o-phenanthroline ferrous sulfate as an indicator. The ceric sulfate solution was standardized against Oesper's salt. The per cent reducing material in the sample is then calculated.

For the final calculation of results, let:

A = % total copper

B = % metallic copper

C = % reducing material expressed as Cu_2O.

Then, D = % Cu_2O = C - 2.2616B, where 2.2616 is the factor Cu_2O/Cu, and % CuO = $[A - (B + 0.8882D)]/1.2517$, where 0.8882 is the factor $2Cu/Cu_2O$ and 1.2517 is the factor CuO/Cu.

According to this method of analysis, the cuprous oxide preparation analyzed:

Cu = 2.2%

Cu_2O = 64.1%

CuO = 26.4%

Unaccounted for = 7.3%.

This material will hereafter be referred to as Cu_2O.

Analysis of vanadium tetroxide preparation

Although Stewart (64) first used V_2O_4 as a promoter, and both Stanerson (63) and Lefrancois (40) studied its catalytic effects, the material had not been analyzed. Lefrancois (40, p. 40), stated that, by comparison with various statements in the literature, the preparation is probably hydrated and contains some unreduced vanadium pentoxide.

As a first attempt at analyzing the preparation, several samples were dissolved in dilute sulfuric acid in a CO_2 atmosphere according to the method of Prandtl and Murschhauser (55). According to this method, a weighed sample of the preparation is placed in a stoppered Erlenmeyer flask and covered with dilute H_2SO_4. A saturated solution of $NaHCO_3$ is then introduced through a dropping funnel inserted in the stopper in the flask. The carbon dioxide thus generated displaces the air in the flask and provides a non-oxidizing atmosphere. The mixture is then warmed until all of the sample has dissolved. The pentavalent vanadium content of the resulting solution was determined according to the procedure recommended by Ransey (56).

After the solution has cooled, a solution of 2 g. of KI in 50 ml. of H_2O is added through the dropping funnel. This made the resulting solution about 3 N in H_2SO_4. After complete reduction of the pentavalent vanadium present, the solution is

diluted to 200 ml., a buret is inserted in the stopper and the I_2 liberated by the reduction is titrated with standard sodium thiosulfate solution, using starch as an indicator. However, the results given by this method were unsatisfactory. Below are presented some results given by this procedure:

	$\%V_2O_5$
Sample I	82.94
Sample II	78.57
Sample III	75.76
Sample IV	74.02.

It was found, however, that the method of Morette and Gaudefroy (49) gave good results. This method consists in weighing a 0.05 g. sample into an Erlenmeyer flask and then covering the sample with a thin layer of a saturated solution of sodium bicarbonate. The sample is then dissolved by adding 20 to 30 ml. of 9 N H_2SO_4 and then stirring and crushing the sample until it completely dissolves. Then 40 to 60 ml. of H_2O and 5 ml. of H_3PO_4 (D = 1.61) are added.

The indicator used is oxidized diphenylaminesulfonic acid prepared according to the directions given by Willard and Diehl (76). Four drops of diphenylaminesulfonic acid solution are placed in a 30 ml. beaker, 5 drops of H_2O, 5 to 6 drops of N/50 $FeSO_4$ solution, 3 to 4 drops of conc. H_2SO_4 and 3 to 4 drops of N/10 $K_2Cr_2O_7$ are added. From a buret, N/50 $FeSO_4$ is added until the purple color of the solution just turns to bluish-green. The resulting solution is then

added to the flask containing the vanadium solution. The pentavalent vanadium in this solution is then determined by titration with a standard N/50 $FeSO_4$ solution (prepared from primary standard grade ethylenediamine ferrous sulfate).

One gram of solid potassium persulfate is then added to the flask and the mixture boiled on a water bath for 45 minutes to oxidize all the vanadium present to the pentavalent state. After cooling the flask in running water, another portion of the oxidized diphenylaminesulfonic acid indicator is prepared and added to the solution. The total vanadium content of the solution is then determined by titration with standard N/50 $FeSO_4$ solution as before.

By knowing the total vanadium content of the sample and the pentavalent vanadium content, the per cent V_2O_4 can be calculated. This led to the following results:

V_2O_4 = 44.1%

V_2O_5 = 48.2%

Unaccounted for = 7.7%.

This material will hereafter be referred to as V_2O_4.

Analysis of calcium oxide preparation

The total calcium content of the calcium oxide preparation was determined by an adaptation of a method used to determine total hardness in water (19). A weighed sample was dissolved in 3 N HCl, the resulting solution was boiled to expel any carbon dioxide present, then cooled and neutralized

with 3 N NH_4OH. Some NH_4Cl-NH_4OH buffer solution was added, then a small amount of NaCN and finally an indicator solution prepared by dissolving eriochromeschwartz T and hydroxylamine hydrochloride in methanol. The mixture was then titrated with a standard solution of disodium dihydrogen ethylenediamine tetraacetate. This solution was standardized against primary standard grade calcium carbonate. A series of such determinations gave, as an average, 69.84 per cent Ca. Pure CaO contains 71.47 per cent Ca.

An attempt to determine the per cent $CaCO_3$ in the CaO preparation was made. However, the loss of weight method of Scott and Jewell (59, p. 238) did not lead to consistent results with pure $CaCO_3$, so no analysis of the calcium oxide preparation was made. This material will hereafter be referred to as CaO.

Adsorption of Hydrogen

Apparatus

The apparatus used (see Figure 2) was the same as that used by Stanerson (63, p. 19). The only change made in the apparatus was the introduction of a standard taper joint above the catalyst bulb A. This facilitated the changing of samples. During all of the runs made, the joint was made vacuum tight with glyptal.

Procedure

The procedure used was the same as that given by Staner-

son (62, pp. 28-31). The bulb, A, was of about 50 ml. capacity. It was weighed before and after filling with catalyst and then a small wad of cotton was placed above the catalyst to prevent any fine particles from going up into the capillary tubing above the bulb on evacuation. After the bulb was sealed to the system with glyptal, evacuation was started with a water aspirator attached to points V. When this appeared complete, the pumping was continued with an oil pump attached to the apparatus at point L. This pumping was continued over night. At the end of this period, the final evacuation was made with a Toepler pump connected as shown in Figure 2.

After complete evacuation, the air inlets to the mercury reservoirs R, R' and R" were opened to the atmosphere at points P. The mercury did not completely fill the gas buret. The volume of the space between the zero reading of the buret and the stopcocks H and K was determined as follows. If a certain amount of gas (air) is allowed to enter the buret through stopcock K, while stopcock H is closed, and then stopcock K is closed, a certain number of moles of gas, n, are present. If the temperature of the system be kept constant at room temperature and the pressure and volume of the gas changed by lowering or raising the mercury in the buret, the extra volume, x, may be calculated as follows, assuming the perfect gas law holds:

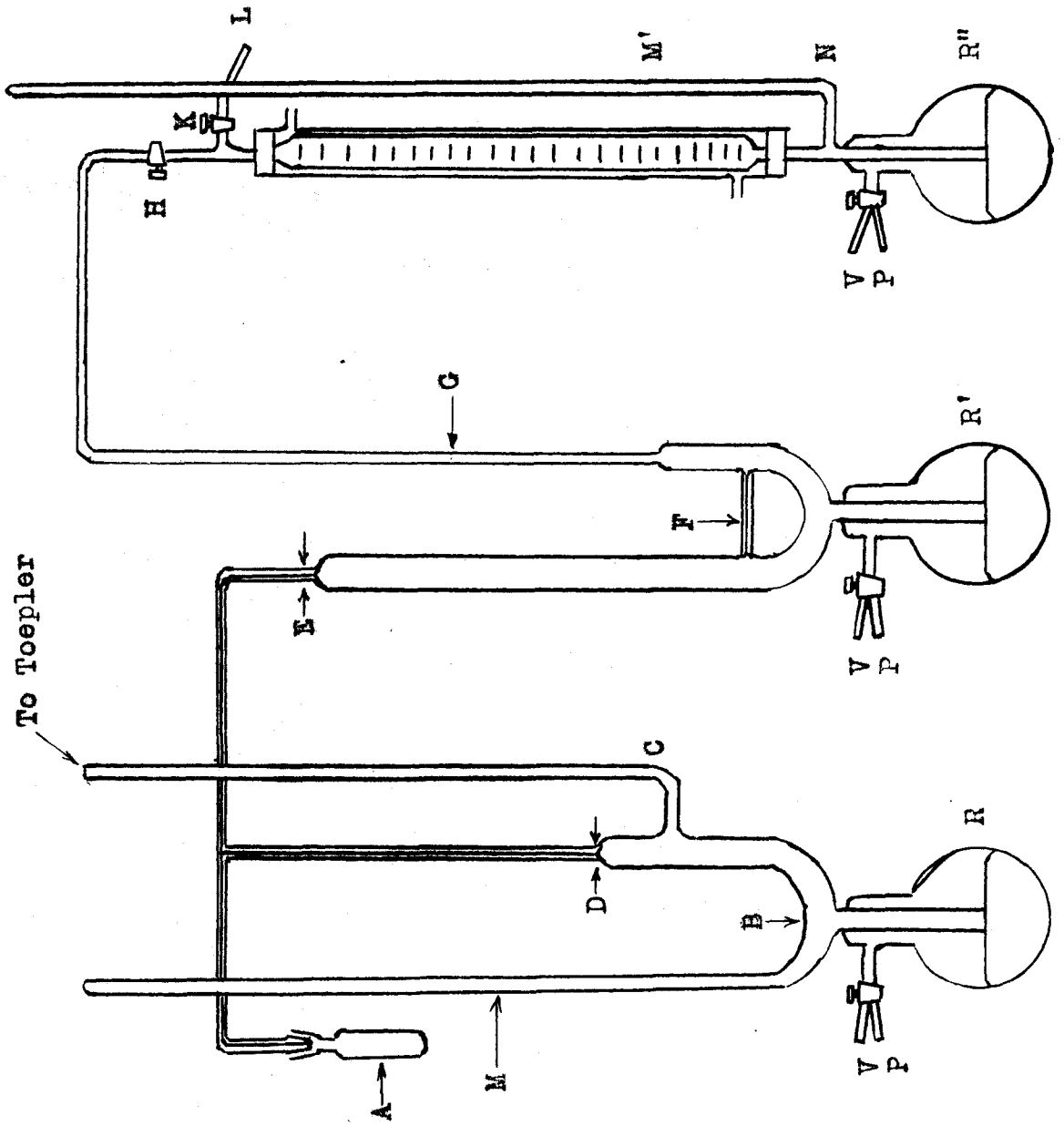


Figure 2: Adsorption apparatus

$$P_1(V_1 + x) = nRT = P_2(V_2 + x)$$

$$x = \frac{P_1V_1 - P_2V_2}{P_2 - P_1}.$$

A series of such measurements gave for the volume, x, a value of 1.99 ml. at standard conditions. This volume was added to each buret reading to give the total volume of gas in the buret.

After the air was removed from the buret, stopcock H was closed and stopcock K opened so the helium could be drawn into the buret from a small cylinder. The helium used was supplied by Matheson Co. and had a purity of 99.8 per cent. When the desired amount of helium had entered the buret, the temperature, pressure and volume were read. All mercury levels were read by means of a cathetometer placed on a table a few feet away from the center of the apparatus.

The next step was to lower the mercury level above R' until it was near the cut-off F, and then stopcock H was opened in order to transfer some of the gas from the buret to the adsorption bulb. After a suitable amount of gas had passed through the cut-off, the pressure on R' was increased until the mercury rose exactly to point E, and to some point in the capillary G. This point varied in position so that a correction had to be made for the various amounts of gas left in G.

Vacuum or pressure was then applied to R until the mercury stood exactly at D. The volume in which the gas was

trapped was then always the same, since it included the bulb and the capillary tubing between points D and E. The pressure of gas in the bulb as well as the pressure and volume of the gas remaining in the buret was then read and from these data the volume of the free space in the bulb could be calculated.

The helium was next pumped out of the system. Tank hydrogen, supplied by Linde Air Products, Inc., was then introduced into the gas buret through stopcock K, where its volume, temperature and pressure were measured. The hydrogen was then transferred to the adsorption bulb. From the difference in the amount of helium necessary to fill the bulb at a certain pressure and the amount of hydrogen necessary to fill the bulb at the same pressure was calculated the amount of hydrogen adsorbed by the catalyst.

The adsorption bulb was surrounded by a beaker containing white mineral oil, a thermometer, stirrer, heating knife and thermoregulator. The temperature of the bath was regulated by means of a Fisher-Serfass electronic relay and could be controlled to ±0.5° C.

Adsorption studies

A sample of catalyst was prepared from 1.0 g. Cu_2O, 0.70 g. V_2O_4 and 1.4 g. CaO. This mixture was transferred to the tared adsorption bulb. The weight of the sample taken was 2.792 g. The bulb was then sealed to the apparatus and the system was pumped out. It was found that the system could not be completely evacuated, but that a relatively con-

stant volume of gas could be removed indefinitely by the Toepler pump. The system was then tested for leaks by means of a Tesla coil. No leaks could be found. The sample was then removed and the empty bulb resealed to the system. The system could then be completely evacuated. Thus the gas being removed from the system was being given off by the catalyst sample. The sample was then replaced in the bulb and the bulb was heated to 100° C. Again, the apparatus could not be completely evacuated. The bulb was then heated to 190° C. Again, the system could not be completely evacuated. On cooling the bulb to room temperature, it was found that the apparatus could be completely evacuated.

The free space in the adsorption bulb was then measured with helium, the helium was pumped out and tank H_2 introduced. The bulb was heated to 100° C. and adsorption allowed to take place at constant temperature. Stanerson (63, p. 36), states that the adsorption of hydrogen started with noticeable velocity at about 57° C. and that the length of time for an adsorption to reach equilibrium at 100° C. was usually about one-half hour. Neither of these observations were confirmed. After 60 hours at 100° C., the adsorption appeared complete. The final pressure in the bulb was 7.79 cm. The volume of hydrogen adsorbed was 14.67 ml. (at standard conditions). The volume of hydrogen adsorbed by enough catalyst to contain 100 g. Cu_2O was 1869 ml. Stanerson (63, p. 42), found about 410 ml.

A desorption experiment was then run on this sample to test the reversibility of the adsorption of hydrogen. The bulb allowed to cool to room temperature (30° C.) over night and then the system was completely evacuated by means of the oil pump and the Toepler pump. The system was then allowed to stand for one-half hour and the pressure was read. The bulb was then heated to 40° C., allowed to stand for one-half hour, and the pressure was then read. This was repeated for each 10° C. rise in temperature over the range 30° C. to 250° C. The results are shown in Figure 3, where the per cent of the hydrogen adsorbed at 100° C. which was desorbed is plotted against temperature.

The bulb was then allowed to cool to room temperature, removed and weighed. It was found that a loss in weight of 0.037 g. occurred during the adsorption and desorption processes. The sample was then analyzed for metallic copper content according to the procedure of Ubaldini and Guerrieri (75). The metallic copper content was found to be 3.2 per cent.

An adsorption experiment was next carried out on a catalyst sample which had never been heated above 100° C. Another sample was prepared from 1.0 g. Cu_2O, 0.70 g. V_2O_4 and 1.40 g. CaO and transferred to the adsorption bulb. The weight of the catalyst transferred was 2.610 g. The bulb was attached to the system and evacuated as before. Once again, it was found very difficult to remove all the gas in the system. After evacuation was as complete as possible, the free

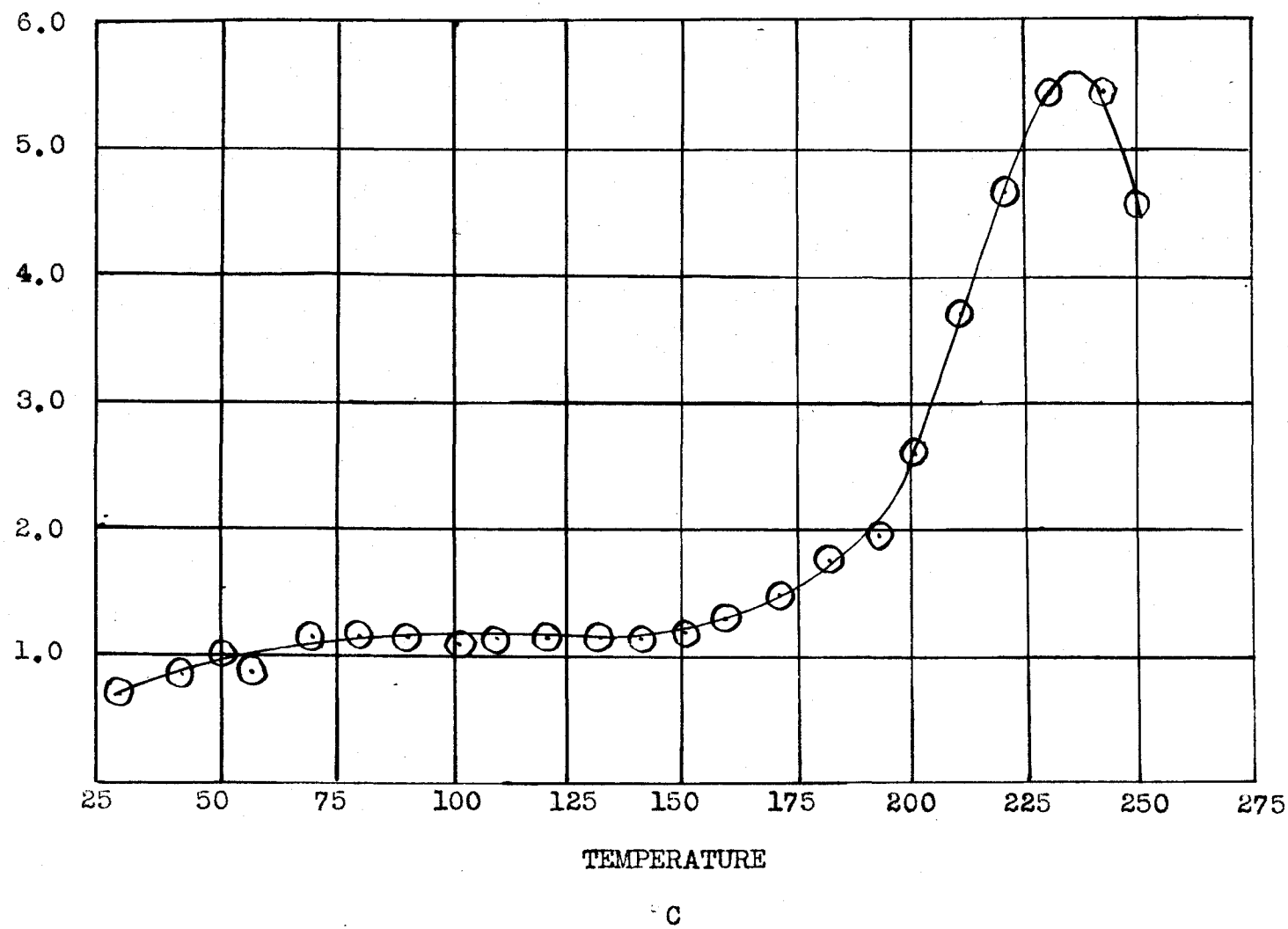


Fig. 3. Desorption of H_2 adsorbed at 100°C.

space in the adsorption bulb was determined with helium. The helium was then pumped out and hydrogen added to the bulb. The bulb was then heated to 100° C. Adsorption was complete after 13 hours. The volume of hydrogen adsorbed was 15.19 ml. The final pressure in the bulb was 0.74 cm. The volume of hydrogen adsorbed by enough catalyst to contain 100 g. of Cu_2O was 1802 ml. Stanerson (63, p. 42) found less than 71 ml.

The system was then allowed to cool to room temperature (30° C.) and evacuated and then allowed to stand over night. After standing, the pressure in the bulb increased 0.04 cm. An increase of only 0.04 cm. in pressure after 16 hours at 30° indicates that a negligible amount of adsorbed hydrogen was lost while evacuating the system. A desorption study was then carried out by heating the system to 50° C., allowing it to stand at this temperature for one hour, at which time the pressure was recorded. This process was repeated, raising the temperature of the bulb 20° C. at a step, until a noticeable desorption occurred. This started at 160° C. The system was kept then at 160° C. while an isothermal rate of desorption experiment was carried out. The data thus obtained are shown in Figure 4, where the per cent of adsorbed hydrogen which was desorbed is plotted against time. The temperature of the system was then dropped from 160° to 100° C. This change in temperature was brought about as rapidly as possible by siphoning off the hot mineral oil in the bath and then adding cold mineral oil. Readings of pressure were

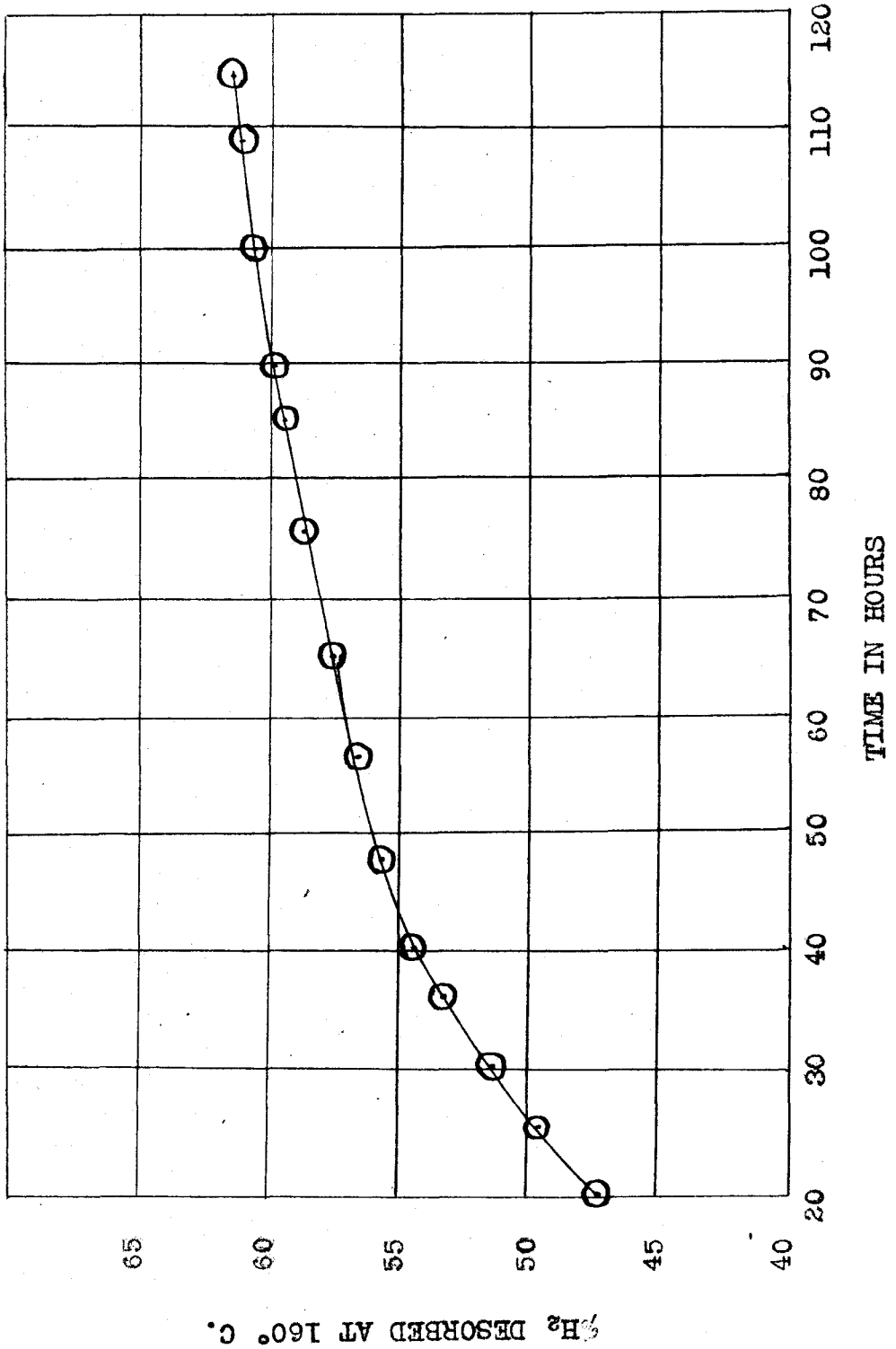


Fig. 4. Isothermal rate of desorption of H_2

taken every hour for seven hours. No readsorption of hydrogen occurred. The system was then cooled to room temperature by standing over night. Again, no readsorption of hydrogen occurred.

The bulb was then removed from the apparatus and the sample of catalyst in the bulb was analyzed for V_2O_4 and V_2O_5 content according to the procedure of Morette and Gaudefroy (49). Accordingly, a weighed sample of the catalyst was placed in a flask, covered with a layer of a saturated solution of $NaHCO_3$ and treated with 9 N H_2SO_4. The undissolved $CaSO_4$ and Cu were filtered off and some oxidized diphenylaminesulfonic acid indicator added. No color change occurred, which means that no pentavalent vanadium was present. This was repeated on another portion of the catalyst with the same results. Next, a fresh sample of the catalyst was prepared from 1.0 g. Cu_2O, 0.70 g. V_2O_4 and 1.40 g. CaO. This was analyzed for pentavalent vanadium content by the same procedure. Again, no change in color occurred on adding the indicator solution. Since the V_2O_4 used in preparing this sample contained 48 per cent V_2O_5, it is apparent that the mixed catalyst cannot be analyzed for pentavalent and tetravalent vanadium content by this method.

Lefrancois (40, p. 33) reported that the use of freshly ignited CaO is very important. Accordingly, some of the CaO was ignited in a porcelain crucible at the full heat of a Meker burner for two hours. It was then placed quickly in a

desiccator over Anhydrone and Ascarite for three hours. A catalyst mixture containing 1.0 g. Cu_2O, 0.70 g. V_2O_4 and 1.40 g. of this CaO was prepared and placed in the adsorption bulb. An adsorption of hydrogen study was made on this sample at 100° C. as before. The weight of sample used was 2.133 g. After adsorption was complete, more additions of hydrogen were made. The results are summarized in Table 2.

TABLE 2

Adsorption of Hydrogen by a Catalyst Sample Containing Freshly Ignited CaO

Addn. No.	Vol. of H_2 adsorbed ml.	Fin. Press. in bulb. cm.	Adsptn. cmplt'd. (time)	Total vol. H_2 adsbd. by sample	Total vol. H_2 adsbd. by eno. cat. to cont. 100 g. Cu_2O
1	15.40 ml.	3.53 cm.	9 hrs.	15.40 ml.	2235 ml.
2	12.76 ml.	3.15 cm.	6 hrs.	28.16 ml.	4087 ml.
3	16.66 ml.	3.05 cm	6 hrs.	44.82 ml.	6505 ml.
4	15.59 ml.	0.43 cm.	4½ hrs.	60.41 ml.	8768 ml.
5	18.27 ml.	0.44 cm.	6 hrs.	78.68 ml.	11419 ml.
6	18.29 ml.	0.47 cm.	6 hrs.	96.97 ml.	14074 ml.

The seventh addition of hydrogen ruined this experiment as the catalyst bulb was accidentally filled with mercury. Rates of adsorption were determined during this series of experiments. The curves obtained are presented in Figure 5.

Next, an attempt was made to saturate the catalyst with hydrogen at 100° C. by the successive addition of portions of

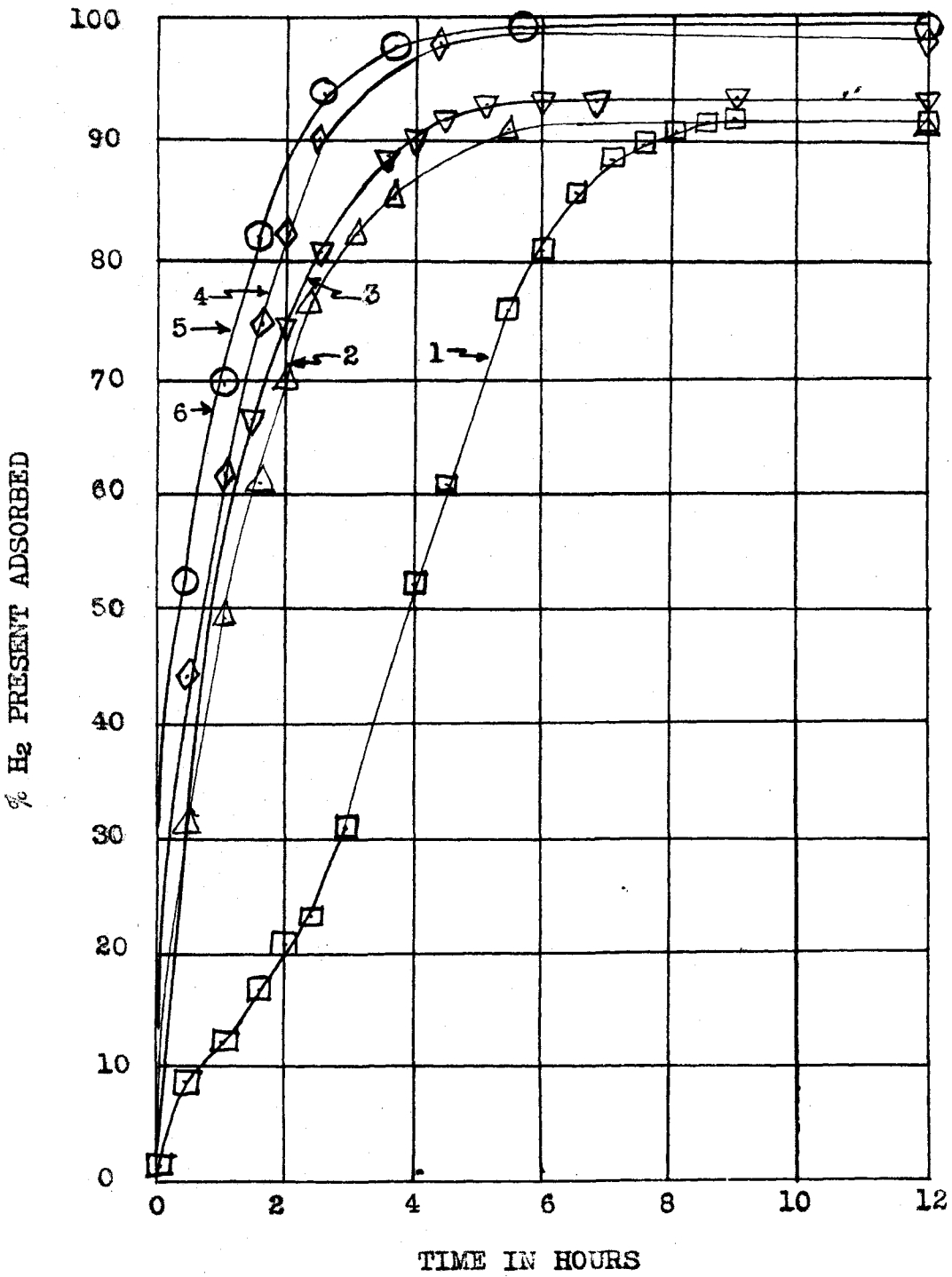


Fig. 5. Rates of adsorption obtained on successive additions of portions of H_2.
The numbers refer to the sequence of addition.
Note: curves 5 and 6 coincide.

hydrogen as soon as adsorption of the previous portion appeared to be complete. No rates of adsorption were determined in this series. Another sample of catalyst was prepared from 1.0 g. Cu_2O, 0.70 g. V_2O_4 and 1.40 g. CaO (not freshly ignited). The weight of sample taken was 2.265 g. The results are summarized in Table 3.

TABLE 3

Saturation of the Catalyst with Hydrogen

Addn. No.	Vol. of H_2 adsorbed	Final pressure in bulb	Time allowed for adsptn.	Total vol. of H_2 adsorbed by sample	Total vol. H_2 adsorbed by enough cat. to cont. 100 g. Cu_2O
1	18.24 ml.	0.52 cm.	18 hours	18.24 ml.	2496 ml.
2	18.12 ml.	0.94 cm.	4 hours	36.36 ml.	4976 ml.
3	17.12 ml.	0.60 cm.	18 hours	53.48 ml.	7320 ml.
4	16.80 ml.	0.49 cm.	20 hours	70.28 ml.	9629 ml.
5	17.32 ml.	0.77 cm.	8 hours	87.60 ml.	11,989 ml.
6	17.08 ml.	0.46 cm.	14 hours	104.68 ml.	14,326 ml.
7	16.52 ml.	1.52 cm.	10 hours	121.20 ml.	16,589 ml.
8	5.85 ml.	30.88 cm.	24 hours	127.05 ml.	17,388 ml.
9	1.34 ml.	46.98 cm.	23 hours	128.39 ml.	17,572 ml.

Hydrogen was then removed from the bulb in a series of steps. After each removal, the system was maintained at 100° C. until equilibrium was reached. The results are presented in Table 4.

TABLE 4

Determination of the Volume of Hydrogen Adsorbed by the Catalyst at 100° C. and Various Pressures

Step No.	Vol. of H_2 adsorbed	Final pressure in bulb	Time system kept at 100° C.	Total vol. of H_2 adsorbed by sample	Total vol. H_2 adsorbed by enough cat. to cont. 100 g. Cu_2O
1	1.04 ml.[1]	32.21 cm.	88 hours	129.43 ml.	17,714 ml.
2	0.21 ml.[1]	23.47 cm.	29 hours	129.64 ml.	17,743 ml.
3	-0.05 ml.	15.48 cm.	37 hours	129.59 ml.	17,737 ml.
4	0.13 ml.	9.71 cm.	73 hours	129.72 ml.	17,754 ml.
5	-0.14 ml.[2]	5.31 cm.	45 hours	129.58 ml.	17,735 ml.
6	-0.17 ml.[2]	1.10 cm.	24 hours	129.41 ml.	17,711 ml.
7	-0.01 ml.	0.54 cm.	9 hours	129.40 ml.	17,710 ml.
8	-0.04 ml.	0.53 cm.	11 hours	129.36 ml.	17,705 ml.
9	-0.14 ml.	0.63 cm.	25 hours	129.22 ml.	17,686 ml.

[1] Adsorption was still occurring at a very slow rate.

[2] Desorption was still occurring at a very slow rate.

In steps no. 7, 8 and 9, all the unadsorbed hydrogen in the system was removed as rapidly as possible by pumping with a vacuum pump, which took about 15 minutes. The system was then allowed to stand at 100° C. for the period of time indicated in the table. It is seen that the pressure builds back up to about 0.5 cm.

The hydrogen left in the system after step 9 was then removed by pumping with the Toepler pump. After 10 minutes of

pumping, all the gas appeared to have been removed, so the mercury levels were brought back to the constant volume marks, D and E, Figure 2. The pressure in the bulb then measured 0.32 cm. Evidently all the gas had not been removed, so the Toepler pump was again employed. This time the pressure was 0.17 cm., but as the pressure readings were being taken, the pressure suddenly jumped to 0.32 cm. It would appear that a rapid evolution of adsorbed H_2 occurs on decreasing the pressure below about 0.32 cm.

With the system in this condition, a desorption experiment was stated. The temperature of the bulb was slowly increased until the temperature reached 150° C. Pressure readings were taken for every 2 or 3° rise in temperature. By the time the bulb had reached a temperature of 150° C., 0.15 per cent of the adsorbed hydrogen present had been desorbed. The system was then kept at 150° C., 160° C. and 170° C. for varying periods of time. The results are presented in Table 5.

Between 30 and 96 hours at 190° C., the pressure in the system slowly decreased, due to either readsorption or reaction of the hydrogen present. The catalyst was then removed from the bulb and analyzed for metallic copper. The per cent metallic copper found was 20.2. The per cent originally present was 2.2.

TABLE 5

Desorption of Hydrogen from the Catalyst after Saturation with Hydrogen

Temperature of bulb	Time bulb was kept at this temperature	Final pressure in bulb	Vol. of H_2 desorbed	% H_2 present desorbed
150°	68 hours	14.80 cm.	4.53 ml.	3.51%
160°	4 hours	15.08 cm.	4.69 ml.	3.64%
170°	44 hours	19.86 cm.	5.81 ml.	4.50%
170°[1]	65 hours	3.88 cm.	1.13 ml.	5.15%
180°	72 hours	5.51 cm.	1.61 ml.	5.53%
190°	96 hours	6.08 cm.	1.70 ml.	5.60%

[1] After 44 hours at 170° C., the desorbed hydrogen which had accumulated was pumped off. The bulb was then maintained at 170° C. for an additional 65 hours.

Adsorption of Furfural Vapor

Apparatus

The apparatus used in studying the adsorption of furfural was designed as a modification of the familiar Abderhalden drying pistol. The apparatus is shown in Figure 6. Flask A contained a liquid which was refluxed. The vapors of this liquid pass through the jacket and enter a condenser placed in the standard taper B. The vapors are condensed and the liquid is returned to flask A by means of the tube C. In this manner, the inner chamber D is maintained at a temperature close to the

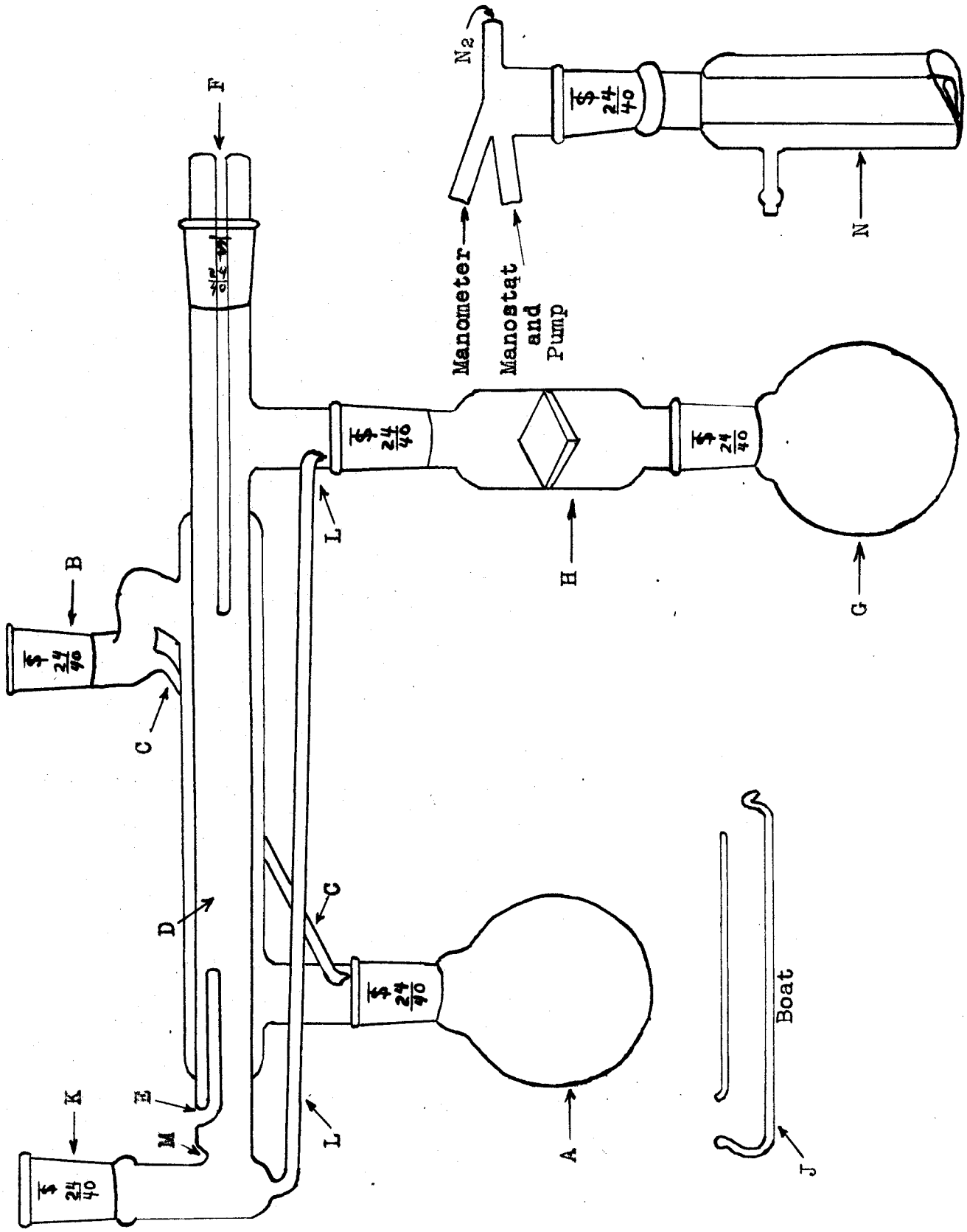


Figure 6. Adsorption apparatus

boiling point of the liquid placed in flask A. The temperature in the inner chamber D was measured by means of a pair of thermocouples inserted in the thermocouple wells E and F.

Flask G contained furfural. When brought to boiling, the furfural vapors passed through the Iowa State type Kjeldahl trap H which caught any liquid furfural which might have bumped up into the trap. The furfural vapors then entered the inner chamber D and passed over the boat J which contained the catalyst sample under study. The vapors of furfural then entered a condenser N placed in the standard taper K. The vapors were then condensed and returned to flask G by means of the tube L. The condensed furfural was prevented from running back into the inner chamber D by means of a crease M in the glass. It was found advisable to place a ring of asbestos paper around the neck of flask A to prevent overheating of the tube L by the burner under flask A.

In the top of the condenser N was placed a Y joint which was connected with a manometer, a N_2 tank and a Cartesian manostat and water aspirator or vacuum pump. The liquid placed in flask A was chosen according to its boiling point and stability on refluxing so that the inner chamber D would be maintained at a temperature above the boiling point of furfural at the pressure being used.

Procedure

The procedure used was to place a weighed sample of the catalyst in the boat J, which was then placed in the inner

chamber D. The system was evacuated and then filled with tank nitrogen. Freshly distilled furfural was placed in flask G and a suitable liquid introduced into flask A. Boiling stones were also placed in flask A to facilitate boiling. Considerable difficulty was experienced with bumping of the furfural, particularly at pressures below atmospheric. The use of boiling stones and wooden applicator sticks failed to prevent bumping. Packing the flask with glass wool also failed as did the introduction of a fine stream of N_2 bubbles. This difficulty was finally overcome by the use of an ebbulator tube of the type recommended by Matviok (43). This is a tube made from thin-walled glass of 2-3 mm. bore. The overall length of the tube is such that, when the lower end rests on the bottom of the flask, the upper end is supported by the neck of the flask. About 10 mm. from the lower end, a section of the tube is sealed off.

The pump was then turned on and when the pressure had reached the desired value, as read on the manometer, the Cartesian manostat was set to maintain that pressure. The liquid in flask A was then boiled. When the temperature of the inner chamber had become constant, as shown by means of thermocouples inserted in the wells E and F, the furfural in flask G was heated to boiling and furfural vapors passed over the catalyst.

After the furfural vapors had passed over the catalyst for some definite period of time, usually an hour, the burner under flask G was turned off. When liquid furfural stopped flowing

from the end of tube L, the burner under flask A was turned off. When the system had cooled to room temperaure, it was brought to atmospheric pressure with N_2 and the pump turned off.

The boat was then removed from the chamber D by means of a length of wire with a hook on one end which engaged a hook on one end of the boat. The boat was then weighed and any change in weight was recorded. The boat was then re-introduced into the chamber and the procedure repeated.

Adsorption studies

The first adsorption study on furfural was made at atmospheric pressure. A sample of the catalyst was prepared from 1.0 g. Cu_2O, 0.70 g. V_2O_4 and 1.40 g. CaO. The weight of sample taken was 3.077 g. The boat was placed in the adsorption apparatus and benzaldehyde (boiling point, 179° C.) was placed in flask A. When the temperature of the inner chamber had reached 179° C., the burner under flask C was turned on. By this time, it was observed that the catalyst had turned black. The usual color of the mixture is dull red. When the furfural vapor entered the adsorption chamber, it condensed to a liquid. While most of this liquid later evaporated, a film of liquid remained between the wall of the boat and the wall of the adsorption chamber. For this reason, the boat was not weighed after removal from the chamber.

The change in color of the catalyst on heating may be due to disproportionation of the Cu_2O present into Cu and CuO. To test this hypothesis, another sample of the catalyst was pre-

pared and divided into two portions. One portion was analyzed for metallic copper content and the other portion placed in the adsorption apparatus and heated by refluxing methyl benzoate (boiling point, 198° C.) for one hour. Again the sample turned black. The system was then cooled in nitrogen and analyzed for metallic copper content. It was found that on heating to 190°, the sample, which weighed 1.645 g., lost 0.030 g. in weight or 1.82 per cent. The portion which had not been heated analyzed 3.40 per cent metallic copper, while the portion which had been heated to 190° analyzed 3.53 per cent metallic copper. Thus, little, if any, disproportionation of cuprous oxide occurred on heating the catalyst to 190° C. in an atmosphere of nitrogen. The loss in weight is probably due to loss of water and the darkening of the catalyst may be due to either pyrolysis of organic matter undoubtedly present or to change in particle size of the catalyst.

Before any further study of the ability of the catalyst to adsorb furfural could be made, it was necessary to know whether the catalyst which had been heated to 190° C. and turned black was still catalytically active. Accordingly, a sample of the catalyst was prepared from 0.70 g. Cu_2O, 0.70 g. V_2O_4 and 0.525 g. CaO. This sample was placed in the boat and heated in N_2 to 190° C. for 3 hours. The sample taken weighed 1.888 g. and lost 0.093 g. or 5.08 per cent by weight on heating. This sample was used to hydrogenate furfural. The results are shown in Figure 7, where the previous hydrogenation run on the unheated catalyst (p. 30) is also given. A comparison of the two curves shows

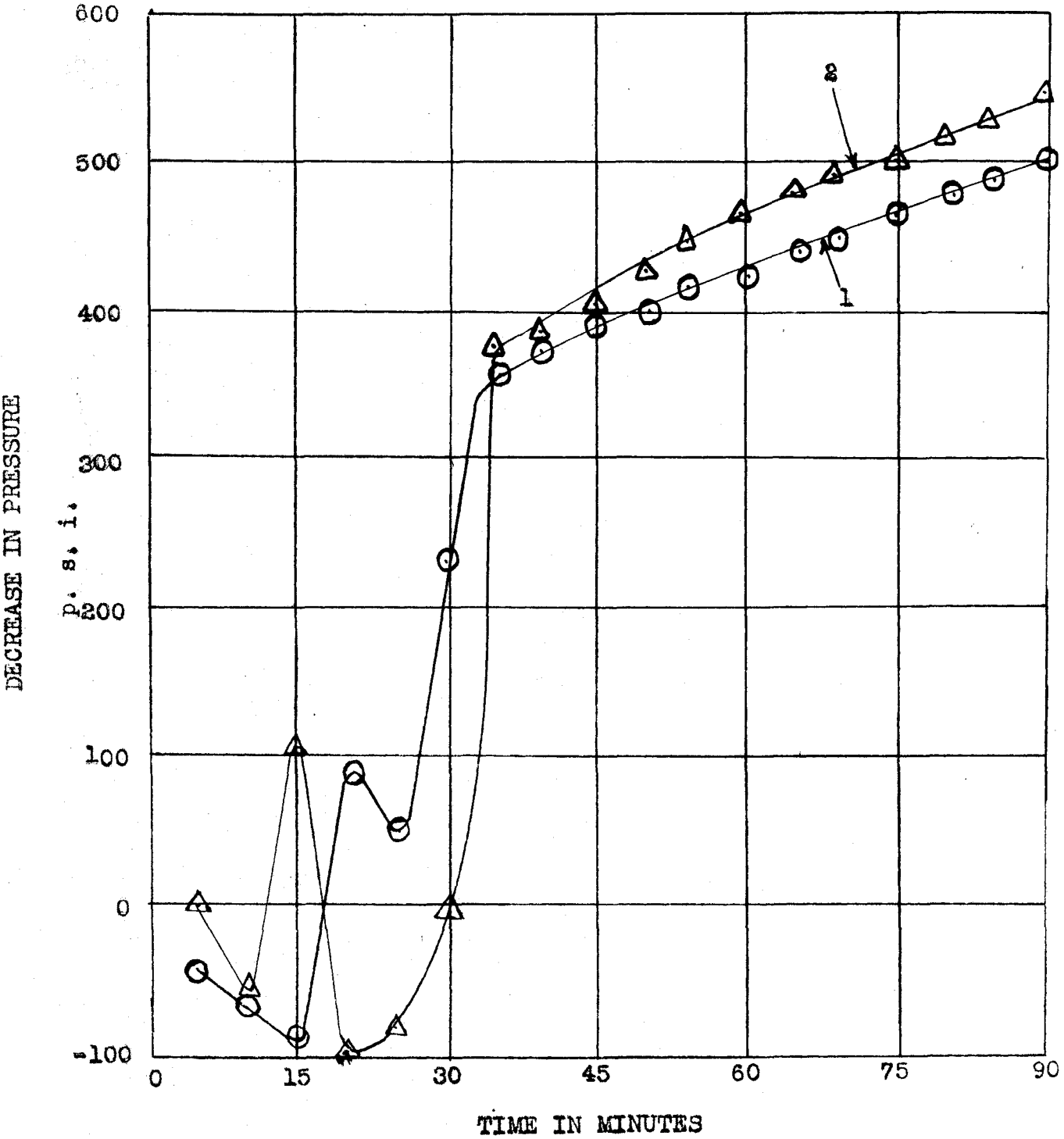


Figure 7. Curve 1, hydrogenation with unheated catalyst
Curve 2, hydrogenation with heated catalyst

that the catalyst which had been heated to 190° C. for 3 hours was catalytically active.

In Figure 7, curve 1 presents the data obtained using an unheated sample of the catalyst. This curve is plotted in greater detail than in Figure 1. It will be noted that between 5 and 15 minutes, the pressure in the bomb increased 93 p. s. i. while the temperature increased from 26° to 73° C. Between 15 and 20 minutes, the pressure decreased 183 p. s. i. while the temperature increased from 73° to 100° C. Between 20 and 25 minutes, the pressure increased 38 p. s. i. while the temperature increased from 100° to 115° C. Thereafter, a smooth decrease in pressure due to reaction followed. Curve 2, Figure 7, presents the data obtained using the heated sample of the catalyst. Between 5 and 10 minutes, the pressure increased 59 p. s. i. while the temperature increased from 23° to 32° C. Between 10 and 15 minutes, the pressure decreased 169 p. s. i. while the temperature increased from 32° to 58° C. Between 15 and 20 minutes, the pressure increased 210 p. s. i. while the temperature increased from 58° to 87° C. Thereafter, a smooth decrease in pressure due to reaction followed.

Another sample of the catalyst was prepared from 1.0 g. Cu_2O, 0.70 g. V_2O_4 and 1.40 g. CaO. The sample was transferred to the boat and weighed. The weight of sample taken was 3.047 g. The boat was then heated by boiling methyl benzoate to 190° in the adsorption apparatus until it came to constant weight.

The sample lost 0.085 g. or 2.78 per cent by weight. This sample was then used to determine the isothermal adsorption characteristics of the catalyst toward furfural vapor at 190 ° and atmospheric pressure. The results are shown in Figure 8 where the increase in weight of the catalyst is plotted against the time the catalyst was exposed to furfural vapor.

Since the rate of adsorption was becoming erratic and more particularly because some of the catalyst was being mechanically transferred by the furfural vapor on past the boat, this run was stopped. The color of the catalyst after adsorption of furfural vapor was a light brown and it was still very powdery. No evidence of the formation of a gummy polymer was noted. Some of thefurfural decomposed on the walls of the adsorption chamber and on the sides of the boat leaving a dark deposit.

The most promising method of analyzing the resulting mixture of catalyst and adsorbed furfural appeared to be that of Maaskant (42). According to this method, furfural may be quantitatively precipitated from its aqueous solution by means of an acetic acid solution of p-nitrophenylhydrazine. It was felt that the adsorbed furfural could best be removed from the catalyst by extraction with anhydrous ether.

In order to test this method of separation and analysis, a synthetic mixture was prepared by treating a sample of the catalyst with a known weight of double-distilled furfural. The mixture was then extracted with anhydrous ether in a Soxhlet apparatus. After four hours of extraction, 94 per cent of the

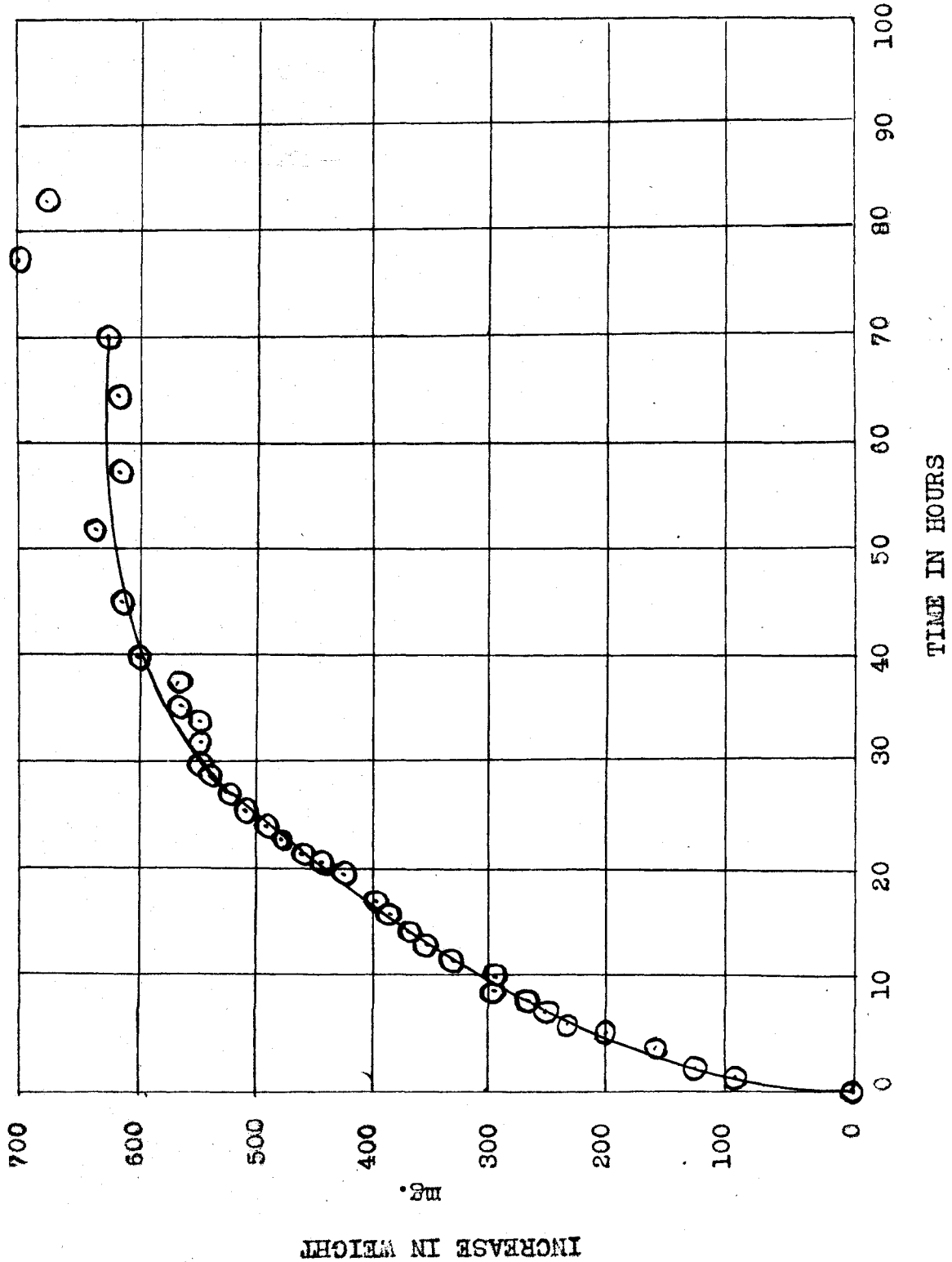


Figure 8. Adsorption of furfural vapor

furfural had been removed from the catalyst. A solution of p-nitrophenylhydrazine was then added to the ether extract, the resulting precipitate was filtered off, washed with water and dried at 110° C. to constant weight. The furfural thus recovered amounted to only 70 per cent of the weight of furfural taken.

Several variations of this method of analysis were tried. The method finally evolved was as follows: the mixture of catalyst and furfural was placed in a Soxhlet extraction thimble and extracted with anhydrous ether for at least 24 hours. At the end of this period, 50 ml. of distilled water was added to the ether extract and a Y-joint attached to the flask. The Y-joint was connected to a nitrogen tank, a manometer and a water pump. The ether layer was then evaporated at room temperaure under reduced pressure. When all the ether had been removed, the flask was filled with N_2. The aqueous furfural solution left in the flask was made 30 per cent in acetic acid, poured into a beaker and the flask was rinsed with 30 per cent acetic acid. A solution containing twice the theoretical amount of p-nitrophenylhydrazine in 30 per cent acetic acid was then prepared and added to the furfural solution. This mixture was allowed to stand overnight and then the resulting precipitate was filtered, washed with 30 per cent acetic acid and then with water. The filtering crucible containing the precipitate was then placed in a vacuum desiccator until it reached constant weight.

This procedure was then used on the sample of catalyst which had been allowed to adsorb furfural vapors at 190° C. and atmospheric pressure. After 48 hours of continuous extraction with anhydrous ether, the sample of catalyst had lost an amount in weight which corresponded to a removal of 21.1 per cent of the adsorbed furfural. On the addition of a solution of 0.770 g. of p-nitrophenylhydrazine in 50 ml. of 30 per cent acetic acid to the aqueous furfural solution, a precipitate was obtained which weighed only 0.023 g., which corresponded to a recovery of only 1.3 per cent of the adsorbed furfural. The precipitate was red-brown in color and melted at 195-200° C. The precipitate was recrystallized from hot ethanol, and then had a melting point of 203-210° C. The melting point of the p-nitrophenylhydrazone of furfural is 154°. The melting point of p-nitrophenylhydrazine is 157° C.

It is possible that furfural in contact with the catalyst might be changed to either furoin or furil. Some furoin and furil were obtained from Eastman, Kodak and Co. and the corresponding p-nitrophenylhydrazones were prepared according to the directions given by McElvain (46).

A 1×10^{-4} molar solution of p-nitrophenylhydrazine in 95 per cent ethanol was prepared in a 50 ml. volumetric flask. Solutions of the p-nitrophenylhydrazones of furfural furoin, furil and the ether extracted material were prepared in 95 per cent ethanol so that they had about the same intensity of color as the p-nitrophenylhydrazine solution. The four solutions of

the known compounds all appeared yellow, while the unknown solution was different, having a distinct pink tinge in addition to a yellow color. These five solutions were then spectrophotometrically examined using a Cary recording spectrophotometer and 2 cm. cells over the wave length range 225 - 880 millimicrons. The resulting spectral distribution curves are shown in Figure 9.

Since the adsorption of furfural vapor by the catalyst at 190° C. is apparently an irreversible process, a series of experiments was carried out to determine at what temperature reversible adsorption of furfural will occur. The procedure used was to prepare a sample of the catalyst from 1.0 g. Cu_2O, 0.70 g. V_2O_4 and 1.40 g. CaO. The sample was then placed in a tared bulb and weighed. The bulb was then placed in a flask of methyl benzoate and evacuated twice, each time being filled with N_2. The bulb was then heated by refluxing methyl benzoate to constant weight. On cooling, the catalyst was protected by a tube containing Ascarite and Anhydrone.

By means of a long capillary pipette, a known weight of freshly distilled furfural was added to the catalyst and mixed by rotating the bulb. The bulb was then allowed to stand at some fixed temperature, surrounded by some appropriate refluxing liquid, for 3 hours; at the end of which time, the system was evacuated with an oil pump, the bulb being maintained at the same temperature. After one hour of pumping, the bulb was cooled in a N_2 atmosphere and then weighed. This was repeated

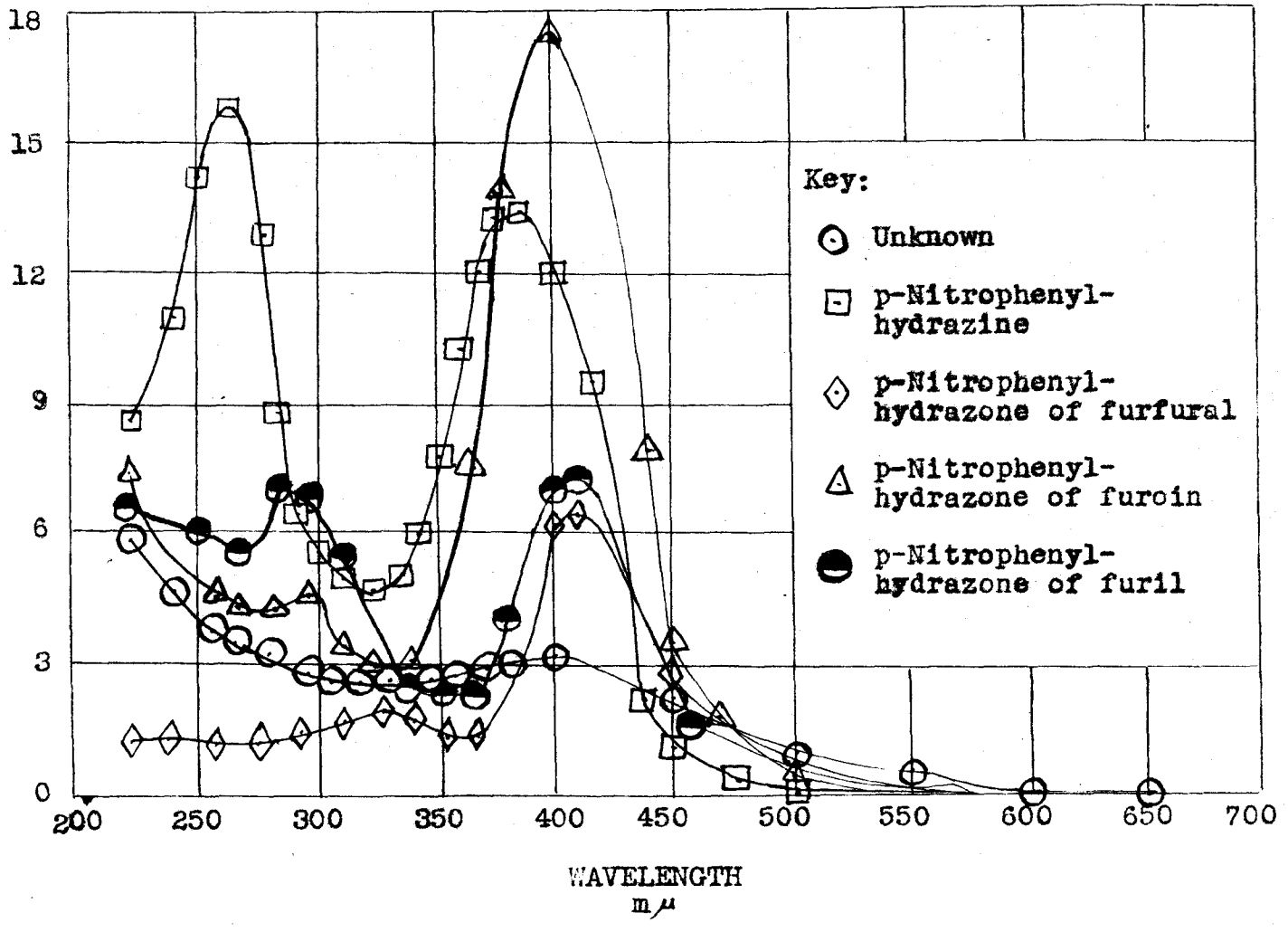


Fig. 9. Spectral distribution curves.

TABLE 6

Determination of the Reversibility of Furfural Adsorption

Wt. of furfural added	Liquid surrounding bulb	Temp. of refluxing liquid	No. of hours of pumping	% furfural removed by pumping
0.935 g.	air	22° C.	22	100.0%
0.711 g.	acetone	55° C.	9	100.0%
0.643 g.	water	100° C.	2	100.0%
0.880 g.	n-amyl acetate	146° C.	6	97.5%
0.689 g.	methyl benzoate	190° C.	4	99.4%

until the bulb reached constant weight. The results are shown in Table 6.

Next, a series of experiments were carried out to determine the adsorption characteristics of the catalyst for furfural at a pressure of 80 mm. and various temperatures. The apparatus and procedure used have already been described (see Figure 6). The results are presented in Table 7.

TABLE 7

Adsorption of Furfural Vapor at 80 mm. Pressure and Various Temperatures

Wt. of catalyst used	Liquid in flask A	Temperature of adsorption chamber	Time of experiment	Increase in weight of catalyst
2.930 g.	water	100° C.	23 hours	0.000 g.
2.900 g.	xylene	136° C.	20 hours	0.000 g.
2.900 g.	bromobenzene	156° C.	6 hours	0.000 g.
2.847 g.	n-butyl n-butyrate	166° C.	11 hours	0.000 g.
2.847 g.	p-cresyl methyl ether	176° C.	6 hours	0.000 g.
2.860 g.	methyl benzoate	190° C.	12 hours	0.175 g.

From Table 7, it is seen that at 80 mm. pressure, no adsorption of furfural vapor occurs until the temperature reaches 190° C. At this temperature at atmospheric pressure, the adsorption of furfural was found to be irreversible, so it is probable that the adsorption of 0.175 g. of furfural at 190° and 80 mm. pressure is also due to an irreversible process.

Adsorption of Furfuryl Alcohol Vapor

Apparatus

The apparatus used was the same as that used in studying the adsorption of furfural (see Figure 6).

Procedure

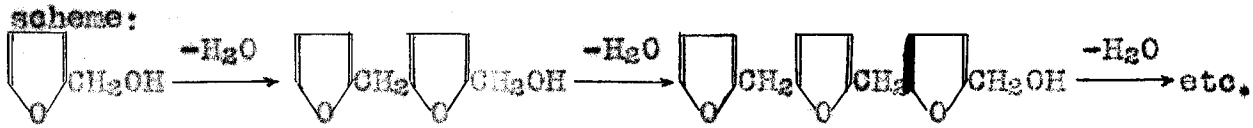
The procedure used was also the same as that used in studying the adsorption of furfural.

Adsorption studies

The first adsorption study on furfuryl alcohol was made at 190° C. and atmospheric pressure. The liquid in flask A was methyl benzoate. A sample of catalyst was prepared from 1.0 g. Cu_2O, 0.70 g. V_2O_4 and 1.40 g. CaO and weighed 2.650 g. The furfuryl alcohol used was obtained from the Paragon Testing Laboratories and was freshly distilled, the first and last portions of the distillate being discarded. The freshly distilled furfuryl alcohol was water white, but it slowly developed a yellow tinge on standing.

Furfuryl alcohol vapor was passed over the catalyst for 11 hours at 190° C. At the end of this time, the catalyst had turned a light tan color and had swollen to several times its original volume, so that it completely clogged the boat. It was found that the catalyst had increased in weight 2.310 g. This relatively enormous increase in weight is indicative of some process other than adsorption.

Dunlop and Peters (20) reported that when furfuryl alcohol is heated, intermolecular dehydration occurs according to the scheme:



Compound I Compound II

They found that after only 3 hours at 200° C., some 20 per cent of the furfuryl alcohol originally present was converted to compound I. Compound I was found to be insoluble in water,

soluble in acetone, benzene and nitrobenzene. The α-naphthyl-urethan derivative of compound I melts at 107-8° C. Compound II exhibited the same solubility characteristics as compound I. However, a Schotten-Baumann test on compound II was unsuccessful.

Thus, the large increase in weight on passing furfuryl alcohol over the catalyst may be due to such an intermolecular dehydration. Furfuryl alcohol is soluble in both acetone and benzene, but benzene was chosen as the solvent with which to extract the catalyst, because part of the vanadium component of the catalyst is soluble in acetone (49) and nitrobenzene has a high boiling point (211° C.) and it was considered undesirable to subject the mixture to any further heating. Thus any unchanged adsorbed furfuryl alcohol as well as any compound I and II present could be separated from the catalyst by benzene extraction. The furfuryl alcohol could then be separated from any compound I or II by taking advantage of the solubility of furfuryl alcohol in water and the insolubility of compounds I and II in water.

The catalyst was therefore transferred to a Soxhlet thimble and extracted with benzene until the extract was colorless, which took about 40 minutes. The benzene extract was red-orange in color. The benzene remaining on the catalyst after extraction was removed by placing the thimble in a beaker and placing both in a drying oven at 110° C. On cooling in air, a thick, yellow-green smoke poured out of the thimble, the catalyst turned jet-black and glowed with burning embers. Enough heat was developed

to char the thimble. Of course, it was now useless to weigh the thimble, so the amount of material removed from the catalyst by benzene extraction is unknown.

The benzene extract was subjected to distillation at atmospheric pressure to remove benzene. A small amount of a dark liquid remained behind. This was poured into a 25 ml. buret and the flask was rinsed with 10 ml. of H_2O which was added to the buret. The mixture was shaken and allowed to stand until it separated into two layers. Deriaz, Stacey, Teece and Wiggins (18) reported that furfuryl alcohol gives a blue color when treated with Dische's reagent which is suitable as a qualitative and semi-quantitative test for furfuryl alcohol. Dische's reagent was prepared according to the procedure given by Sevag, Smolens and Lackman (61). One microspatula of diphenylamine was placed in a test tube, 3 drops of conc. H_2SO_4 and 6 ml. of glacial acetic acid were added. Three ml. of the aqueous layer was added from the buret and the mixture was heated for 3 minutes in a briskly boiling water bath and then cooled under running water. A pale blue color developed which proved the presence of a little furfuryl alcohol. An equal volume of Dische's reagent was prepared in the same manner and 1 drop of furfuryl alcohol added to it. An intense deep blue color developed.

Next the two layers in the buret were separated by draining off the bottom aqueous layer and the non-aqueous layer was placed in a vacuum desiccator over Anhydrone over night. The

next morning the residue was treated with α-naphthylisocyanate according to the procedure given by Shriner and Fuson (62), but no α-naphthylisocyanate derivatives were recovered.

Next, a series of experiments was made to determine the reversibility of furfuryl alcohol adsorption at various temperatures. The procedure and apparatus used were the same as that already described in the case of furfural except for the inclusion in the system of a sintered glass manostatic valve for maintaining an inert atmosphere, as described by Cavagnol (11). The results are shown in Table 8.

TABLE 8

Determination of the Reversibility of Furfuryl Alcohol Adsorption

Wt. of catalyst taken	Wt. of furfuryl alcohol taken	Liquid surrounding bulb	Temp. of refluxing liquid	No. of hours of pumping	% furfuryl alcohol removed by pumping
2.705 g.	0.245 g.	air	28° C.	66	100.0%
2.705 g.	0.424 g.	acetone	55° C.	19	100.0%
2.705 g.	0.360 g.	water	98° C.	3	87.2%
2.770 g.	0.427 g.	CCl_4	75° C.	4	79.5%

Since the adsorption of furfuryl alcohol is to some extent irreversible even at a temperature as low as 75° C., the adsorptive characteristics of the catalyst toward furfuryl alcohol were not further investigated.

Attempted Preparation of Pure Cuprous Oxide

As discussed earlier, it has been shown that the reduction of a solution of $Cu(NO_3)_2$ by glucose followed by the addition of NaOH led to the formation of a cuprous oxide preparation of the composition: Cu, 2.2%; Cu_2O, 64.1%; CuO, 26.4%; unaccounted for, 7.3%. Moser (50) reported a method of preparing Cu_2O by the reduction of a cupric salt with hydroxylamine hydrochloride in a basic solution according to the equation:

$$2Cu^{++} + 2NH_2OH \cdot HCl + 6OH^- = Cu_2O + N_2 + 7H_2O + 2Cl^-.$$

Inasmuch as the oxidation product of the reducing agent is a gas (N_2) and the reducing agent itself is quite soluble in water, as distinct from the case of glucose, the method of Moser appeared to be better suited to the preparation of uncontaminated Cu_2O. The procedure used was as follows: 9.7 g. $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in 90 ml. H_2O and placed in a 500 ml. 3-necked flask equipped with a stirrer, a N_2 inlet and an addition funnel. A solution of 4.5 g. $NH_2OH \cdot HCl$ in 25 ml. H_2O was added to the copper solution. The flask was then surrounded by an ice bath and the stirrer and flow of N_2 started. A solution of 10 g. of KOH in 185 ml. of H_2O was added dropwise with constant stirring.

A bright yellow precipitate formed. It was washed by decantation with water until it peptized. It was then filtered on a Buchner funnel with suction and washed with water until the filtrate gave a negative test for chloride ion. The precipitate was then washed several times with 95 per cent

ethanol and then with acetone. It was then placed in a vacuum desiccator over Anhydrone. After 48 hours, the orange-brown solid was transferred to a weighing bottle. The yield was 2.600 g. or 90.6 per cent of the theoretical. The preparation was then analyzed as before. The analysis gave the following results:

Cu	= 23.0%
Cu_2O	= 44.4%
CuO	= 32.3%
unaccounted for	= 0.3%

In the next attempt to prepare pure cuprous oxide, a non-aqueous solvent was employed to suppress disproportionation of cuprous oxide as much as possible. Seidel (60) lists the following solubilities in methanol:

$CuCl_2$	58.6 g. in 100 g. CH_3OH at 20° C.
$NH_2OH \cdot HCl$	16.4 g. in 100 g. CH_3OH at 20° C.
LiOH	slightly soluble
LiCl	43.8 g. in 100 g. CH_3OH at 20° C.

Accordingly, the following solutions were prepared: 18.8 g. $CuCl_2$ in 100 ml. CH_3OH, 9.7 g. $NH_2OH \cdot HCl$ in 100 ml. CH_3OH, and 17.7 g. $LiOH \cdot H_2O$ in 500 ml. CH_3OH. The solvent used was absolute methanol.

The cupric chloride and hyroxylamine hydrochloride solutions were mixed with stirring in a one-liter, three-necked round-bottomed flask. The lithium hydroxide solution was then added dropwise from a dropping funnel while the solution was constantly stirred and tank nitrogen was bubbled through the

solution. The resulting bright yellow precipitate was filtered on a Buchner funnel and washed with acetone. During the filtering and washing, the precipitate developed a green color. The resulting solid was placed in a vacuum desiccator over Anhydrone until dry. It was then transferred to a weighing bottle. The yield was 9.871 g. or 98.7 per cent of the theoretical. The preparation was then analyzed with the following results:

Cu = 8.4%
Cu_2O = 64.7%
CuO = 12.5%
unaccounted for = 14.4%.

Attempted Preparation of Pure Vanadium Tetroxide

A search of the literature revealed that McCay and Anderson (45) found that when a hydrochloric acid solution of a vanadate is shaken vigorously in the presence of mercury, the solution becomes pure blue in color, the vanadium being quantitatively reduced to the quadrivalent state according to the equation:

$$2HVO_3 + 2Hg + 6HCl = 2VOCl_2 + Hg_2Cl_2 + 4H_2O$$

The following procedure was used: 1.0 g. V_2O_5 was dissolved in 26.6 ml. 9N HCl with boiling. The mixture was cooled and the undissolved material filtered off. The filtrate was caught in a flask which had a ground-glass stopper. Two ml. of mercury were added to the filtrate and the mixture shaken until the solution became pure blue in color. The mixture was then filtered through a sintered glass filter and a solution of 31 g.

K_2CO_3 in 30 ml. of H_2O was added to the filtrate with stirring.

This resulted in the formation of a grey precipitate in a dark red solution. The mixture was filtered, but the precipitate went through the filter. To coagulate the precipitate, the mixture was heated just to boiling, cooled in running water and filtered. Again the precipitate went through the filter. A small portion of the solution was transferred to a test tube and dil. HCl was added dropwise. This resulted in the formation of a blue-grey precipitate, so the solution was too basic. The rest of the solution was treated with dil. HCl with stirring. However, the solution turned green, which is characteristic of pentavalent vanadium in acid solution. A small amount of this green solution was shaken with mercury and the solution turned blue, proof that the vanadium was in the pentavalent state.

Britton and Welford (9) report that when solutions of tetravalent vanadium obtained by the method of McCay and Anderson (45) were titrated with standard base, precipitation began when the solution had reached approximately pH 4. When four equivalents of base had been added, the precipitate changed from greyish-white to dark brown and the supernatant liquid, instead of becoming colorless, assumed a red coloration.

The procedure was then repeated except that solid K_2CO_3 was added to the filtrate until precipitation just began. Then 15 g. of urea was added and the mixture boiled gently for an hour to buffer the solution at pH 4.2 - 4.6, as recommended

by Willard and Furman (77, p. 397) for the precipitation of calcium oxalate. The mixture was then cooled in running water and filtered with suction. The resulting blue precipitate was then washed with water until the filtrate gave a negative test for chloride ion. The precipitate was then washed 3 times with 95 percent ethanol, then 3 times with sodium-dried ether. The resulting light blue-grey solid was then dried in a vacuum desiccator over Anhydrone over night.

By the next morning, the solid had turned a darker blue. The yield was 0.980 g. or 107.3 per cent of the theoretical. Analysis of the preparation gave:

V_2O_5 = 31.1%

V_2O_4 = 50.4%

unaccounted for = 18.5%.

Since the preparation had a definite odor of ethanol, it was dried at 110° C. to constant weight. It was cooled in a desiccator over Anhydrone. The solid turned to a dark blue-black color after heating. It lost 13.3 per cent by weight on heating. Analysis now gave:

V_2O_5 = 73.7%

V_2O_4 = 18.5%

unaccounted for = 7.8%.

Before heating, the ratio $\%V_2O_5/\%V_2O_4$ was 0.62. After heating, this ratio was 4.0. Thus drying in air greatly increased the V_2O_5 content of the preparation.

The next preparation was carried out avoiding contact with

air as much as possible. The shaking with mercury was carried out for one hour and was done mechanically using a windshield wiper. The filtering and washing was done in an oxygen-free atmosphere, oxygen being removed from the air by passage through a vanadous solution, as recommended by Meites and Meites (47). The precipitate was dried to constant weight at 110° C. in a vacuum furnace. The solid analyzed:

V_2O_5 = 31.8%

V_2O_4 = 49.1%

unaccounted for = 19.1%.

Thus, nothing was gained by working in an inert atmosphere. Assuming that the reduction by mercury is quantitative as McCay and Anderson claim, these results might be due to the formation of soluble $HgCl_2$ which, if precipitated on adding base, would analyze as V_2O_5 on titrating with $FeSO_4$ during the analysis. The preparation was analyzed for mercury following the procedure of Willard and Thompson (78) in which mercury is precipitated as the paraperiodate, $Hg_5(IO_6)_2$. However, no mercury was found in the preparation.

The formation of V_2O_5 under oxygen-free conditions might have been due to the presence of peroxides in the ether used to wash the preparation. Accordingly, some of the ether used in the preparation was shaken with an acidified solution of KI. The ether layer turned yellow, proving the presence of peroxides in the ether.

Another preparation was made using the same procedure ex-

cept that the precipitate was not washed with ether. The yield this time was 0.810 g. or 88.8 per cent of the theoretical. The preparation analyzed:

V_2O_5 = 34.9%

V_2O_4 = 48.3%

unaccounted for = 16.8%.

Thus, no improvement was obtained on avoiding the use of ether.

The high fraction of V_2O_5 in the preparation might have been due to incomplete reduction by mercury. Accordingly, the solution was analyzed for pentavalent vanadium after shaking with mercury. However, no pentavalent vanadium was found. Thus the oxidation to the pentavalent state occurs during the precipitation or during the washing and drying to constant weight.

Morette and Gaudefroy (49) recommended the precipitation of V_2O_4 by adding solid $NaHCO_3$ to the vanadyl solution and then making the mixture 80 per cent in acetone. This modification of the procedure resulted in the formation of 0.660 g. of precipitate or 72.4 per cent of the theoretical. The solid analyzed:

V_2O_5 = 2.8%

V_2O_4 = 32.5%

unaccounted for = 64.7%

When the solution was made 80 per cent in acetone, it was noticed that a white precipitate formed, probably NaCl. Accordingly, the preparation was also analyzed for chloride (77,

p. 320) by precipitation as AgCl. The percent NaCl found was 49.4.

Thus washing the precipitate with 80 per cent acetone does not remove NaCl from the preparation.

Another preparation was made. The precipitate was filtered and washed in an atmosphere of tank nitrogen which was bubbled through an alkaline pyrogallol solution to remove traces of oxygen. The precipitate was washed with 200 ml. of freshly boiled distilled water which had been cooled under oxygen-free nitrogen, and then with 200 ml. of acetone. This resulted in the formation of a gelatinous brown precipitate which, when dried in a vacuum oven to constant weight, turned to dark blue crystals. The yield was 0.946 g. or 104 per cent of the theoretical. The preparation analyzed:

V_2O_5 = 1.0%

V_2O_4 = 71.8%

unaccounted for = 27.2%.

It was noticed that when samples of the preparation were treated with 9N H_2SO_4 as the first step in the analysis, bubbles of gas were liberated from the solid. This was probably CO_2 from occluded $NaHCO_3$. The presence of $NaHCO_3$ would also account for a yield greater than 100 per cent. The sample dissolved with difficulty in 9N H_2SO_4; in fact, the mixture had to be boiled to effect complete solution. This may have lead to some re-oxidation of V_2O_4.

Another preparation of pure V_2O_4 was attempted. The only

change in the procedure being the use of a K_2CO_3 solution, boiled and cooled under nitrogen, to bring about the precipitation of V_2O_4. A K_2CO_3 solution was used because the addition of solid $NaHCO_3$ may have resulted in the introduction of air into the vanadyl solution, thus causing oxidation. K_2CO_3 was chosen because it is much more soluble in water than is Na_2CO_3. Thus any occluded K_2CO_3 should be easily removed by washing with water.

The preparation, after drying to constant weight, consisted of dark blue crystals. The yield was 0.863 g. or 94.6 per cent of the theoretical. Analysis gave:

V_2O_5 = 13.1%

V_2O_4 = 71.6%

unaccounted for = 15.3%.

Since this preparation was worse than the last one, the attempts to prepare pure V_2O_4 were terminated.

CONCLUSIONS

In repeating some of the adsorption of hydrogen studies carried out by Stanerson (62), a number of new observations were made. Stanerson had found that a rapid adsorption of hydrogen started at temperatures close to 60° C., and that adsorption was apparently complete after one-half hour at 100° C. Neither of the observations were confirmed. Instead, it was found that adsorption proceeded slowly at 100° C., never becoming complete in less than four hours. It should be pointed out, however, that several important factors were different in the two studies. First of all, Stanerson used a catalyst prepared from 1.0 g. Cu_2O, 0.48 g. V_2O_4 and 0.48 g. CaO, whereas, in the present study, the catalyst used was prepared from 1.0 g. Cu_2O, 0.70 g. V_2O_4 and 1.40 g. CaO. Secondly, Stanerson used carefully purified hydrogen, whereas, the hydrogen used in the present study was taken directly from a tank. Thirdly, Stanerson used a freshly prepared sample of the catalyst which had never been heated above 100° C. before exposure to hydrogen, whereas, in the present study, some samples had been heated to constant weight at 190° C., before adsorption of hydrogen was investigated. However, it was found that such preheating had no particular effect on the adsorptive capacity of the catalyst, whereas the rate of adsorption was profoundly influenced, since it took a preheated sample some 60 hours to adsorb 14.67 ml. of H_2 while another unheated sample of the

catalyst adsorbed 15.45 ml. of H_2 in some 6 hours.

The adsorption of hydrogen was so slow in the present case that rates of adsorption could be measured. In general, the curves obtained are well represented by the familiar exponential type of expression, $dV/dt = kV$. In trying to saturate the catalyst with hydrogen at 100° C., it was found that the greater the amount of hydrogen already adsorbed, the greater the rate of adsorption of the next quantity (see Figure 5). The volume of hydrogen adsorbed was enormous compared to that found by Stanerson.

In one experiment using a Cu_2O-CaO catalyst, Stanerson found that the adsorption of hydrogen was essentially irreversible since only a small fraction of the hydrogen adsorbed at 100° C. could be removed by pumping at 100° C. These desorption experiments were considerably extended in the present study. It was found that when a sample of catalyst which had been preheated to constant weight at 190° C. was allowed to adsorb 14.67 ml. of H_2 at 100° C., only some 6 per cent of this hydrogen could be removed by heating to 250° C. (see Figure 3). On the other hand, another sample of the catalyst which was not preheated and which was allowed to adsorb 15.45 ml. of hydrogen at 100° C., desorbed as much as 63 per cent of the hydrogen at 160° C. (see Figure 4). Thus, while preheating the catalyst did not seem to affect the catalytic activity, it did affect the reversibility of hydrogen adsorption.

The preheated sample was analyzed for metallic copper

content after the desorption experiment, and no significant change was found after the sample had been heated to 250° C. in the presence of adsorbed hydrogen. Thus, the catalyst appears to be well protected against reduction during hydrogenation reactions.

Lefrancois reported that the use of freshly ignited CaO very important. However, no difference could be noted in either hydrogenation rates or adsorption of hydrogen rates between the freshly ignited and an old preparation of CaO. However, the old preparation was well protected since the ignition.

In one experiment, the catalyst was saturated at 100° C. by nine successive additions of hydrogen. On heating as high as 190° C., only 5.6 per cent of this hydrogen desorbed. On analyzing the catalyst after the desorption experiment, a metallic copper content of 20.2 per cent was found, which is some ten times the original metallic copper content of the sample. However, the catalyst had had every chance to be reduced, having been heated 840 hours or 35 days at 100° C. or more in the presence of hydrogen. This particular sample had not been preheated, so it is apparent that while adsorption is reversible on such samples, after a long period of time, the adsorption becomes irreversible. This irreversible adsorption is probably due to reaction of the adsorbed hydrogen with either Cu_2O or V_2O_4 or both to form water, which is picked up by the CaO present. Thus, unless some means is found to distinguish between that hydrogen which has been adsorbed and that hydro-

gen which has reacted with the catalyst, not much significance is to be attached to the adsorption of hydrogen by this catalyst. It is not surprising that Stanerson found only a fair correlation between catalytic activity and adsorptive capacity toward hydrogen in view of the fact that the adsorption he measured was not entirely chemisorption.

In the case of adsorption of furfural and furfuryl alcohol by the catalyst, the situation is more clear-cut. It was found that the catalyst would not adsorb furfural at temperatures below 190° C. At this temperature, adsorption did occur, but it was immediately followed by reaction, since no furfural could be recovered from the catalyst. It was shown that the furfural was not converted to either furoin or furil.

In the case of furfuryl alcohol, it was found that irreversible adsorption occurred at temperatures as low as 75° C., and that most of the furfuryl alcohol is converted to some material which will not form an α-naphthylurethan derivative, in other words, which does not possess an hydroxyl group.

Thus, it may be concluded that the mechanism of the liquid phase hydrogenation of furfural to furfuryl alcohol in the presence of a cuprous oxide catalyst involves the chemisorption of hydrogen, followed by reaction with molecular, unadsorbed furfural to form unadsorbed furfuryl alcohol. Here again is a case of a catalytic reaction in which some of the adsorption steps are missing.

The preparation of pure cuprous oxide was attempted using

a mild inorganic reducing agent in both water and a non-aqueous solvent. In neither case was the resulting preparation any purer than that obtained by glucose reduction, except perhaps in the absence of organic matter. In spite of glowing reports of earlier workers in the literature, it is to be doubted seriously whether pure cuprous oxide has ever been prepared from solution at low temperatures.

Several attempts to prepare pure vanadium tetroxide failed. Even though precautions were taken to assure complete reduction to the tetravalent state before precipitation, and contact with air was avoided during all the filtering, washing and drying steps, the best preparation obtained still contained 1.0 per cent V_2O_5.

SUMMARY

1. The adsorption of hydrogen by a cuprous oxide catalyst, promoted by V_2O_4 and CaO, has been reinvestigated and it was found that the adsorption is irreversible and complicated by reduction of the catalyst.

2. The adsorption of furfural by the catalyst was found not to occur except at high temperatures where the furfural is converted to some other material which is neither furoin nor furil.

3. The adsorption of furfuryl alcohol by the catalyst was found to be irreversible at temperatures as low as 75° C. and it was found that most of the furfuryl alcohol is converted to some non-hydroxyl containing material.

4. Attempts to prepare pure Cu_2O by precipitation both from aqueous and non-aqueous media failed.

5. Attempts to prepare pure V_2O_4 by precipitation from a pure vanadyl solution failed to yield a product free from V_2O_5.

LITERATURE CITED

1. Adkins, H. Reactions of Hydrogen with Organic Compounds over Copper-Chromium Oxide and Nickel Catalysts. p. 13. Madison, Wis. University of Wisconsin Press. 1937.

2. Barker, R. L., Booth, E., Jones, W. E. and Woodward, F. N., J. Soc. Chem. Ind. (London), 68, 277 (1949).

3. Benton, A. F., J. Am. Chem. Soc., 45, 900 (1923).

4. Benton, A. F. and Bell, R. T., J. Am. Chem. Soc., 56, 501 (1934).

5. Benton, A. F. and Drake, L. C., J. Am. Chem. Soc., 56, 255 (1934).

6. Benton, A. F. and Elgin, J. C., J. Am. Chem. Soc., 48, 3027 (1926).

7. Benton, A. F. and Elgin, J. C., J. Am. Chem. Soc., 49, 2426 (1927).

8. Benton, A. F. and Elgin, J. C., J. Am. Chem. Soc., 51, 7 (1929).

9. Britton, H. T. S. and Welford, G., J. Chem. Soc., 1940, 758.

10. Brunauer, S. and Emmett, P. H., J. Am. Chem. Soc., 62, 1732 (1940).

11. Cavagnol, J. C., Anal. Chem., 21, 760 (1950).

12. Conner, R., Folkers, K. and Adkins, H., J. Am. Chem. Soc., 54, 1138 (1932).

13. Crawley, B. and Griffith, R. H., Trans. Faraday Soc., 32, 1623 (1936).

14. Crawley, B. and Griffith, R. H., J. Chem. Soc., 1938, 2034.

15. Craxford, S. R., Trans. Faraday Soc., 35, 946 (1939).

16. Day, B. B., Govindachari, T. R. and Venkatakrishna, H., J. Sci. Ind. Research (India), 1B, 25 (1946).

17. de Loisy, E. and Damiens, A., Chimie et industrie, Special No., 664 (1923). (Original not available for examination; abstracted in Chem. Abst., 17, 3318. 1923.)

18. Deriaz, R. E., Stacey, M., Teece, E. G. and Wiggins, L. F., J. Chem. Soc., 1949, 1222.

19. Diehl, H., Goetz, C. A. and Hach, C. C., J. Am. Water Works Assoc., 42, 40 (1950).

20. Dunlop, A. P. and Peters, F. N., Ind. Eng. Chem., 34, 814 (1942).

21. Emmett, P. H. and Brunauer, S., J. Am. Chem. Soc., 55, 1738 (1933).

22. Emmett, P. H. and Brunauer, S., J. Am. Chem. Soc., 56, 35 (1934).

23. Emmett, P. H. and Kummer, J. T., J. Chim. Phys., 47, 67 (1950).

24. Farkas, L., Chemistry and Industry, 53, 491 (1934).

25. Finkelstein, V. S., Rubanik, M. Ya. and Krizman, I., J. Phys. Chem. (U. S. S. R.), 3, 425 (1932).

26. Frankenburger, W. and Hodler, A., Trans. Faraday Soc., 28, 229 (1932).

27. Garner, W. E. and Kingman, F. E. T., Trans. Faraday Soc., 27, 322 (1931).

28. Gould, A. J., Bleakney, W. and Taylor, H. S., J. Chem. Phys., 2, 362 (1934).

29. Griffith, R. H. The Mechanism of Contact Catalysis. 2d ed. p. 9. London, England. Oxford University Press. 1946.

30. Griffith, R. H. and Hill, S. G., J. Chem. Soc., 1938, 717.

31. Harker, G., J. Soc. Chem. Ind. (London), 51, 323 (1932).

32. Hearne, G. W. and Adams, M. L. U. S. Patent 2,451,350. Oct. 12, 1948. Abstracted in Chem. Abst. 43: 2222. 1949.

33. Hedges, E. S. and Myers, J. E., J. Chem. Soc., 125, 1282 (1924).

34. Horiuti, J., Ogden, G. and Polanyi, M., Trans. Faraday Soc., 30, 663 (1934).

35. Hoskins, W. M. and Bray, W. C., J. Am. Chem. Soc., 48 1454 (1926).

36. Howard, J. and Taylor, H. S., J. Am. Chem. Soc., 56, 2259 (1934).

37. Hurst, W. W. and Rideal, E. K., J. Chem. Soc., 125, 694 (1924).

38. Ingsley, E. G., J. Phys. Chem., 39, 623 (1935).

39. Kurtenacker, A. and Werner, F., Z. anorg. u. allgem. Chem., 160, 333 (1927).

40. Lefrancois, P. A. Cuprous Oxide as a Catalyst: The Effect of Varying the Proportions of Promoter and Stabilizer. Unpublished Ph. D. Thesis. Ames, Iowa, Iowa State College Library. 1944.

41. Leger, A. E. and Ouellet, C., Can. J. Research, 28B, 358 (1950).

42. Maaskant, L., Rec. trav. chim., 55, 1068 (1936).

43. Matviak, M., Chemist-Analyst, 40, 3, 64 (1951).

44. Maxted, E. B. and Moon, C. H., Trans. Faraday Soc., 32, 1375 (1936).

45. McCay, L. W. and Anderson, W. T., J. Am. Chem. Soc., 44, 1018 (1922).

46. McElvain, S. M. The Characterization of Organic Compounds, p. 199. New York. The Macmillan Co. 1946.

47. Meites, L. and Meites, T. S., Anal. Chem., 20, 984 (1948).

48. Menzel, R. E. Catalytic Hydrogenation of Furfural in the Liquid Phase at Various Temperatures and Pressures. Unpublished Ph. D. Thesis. Ames, Iowa, Iowa State College Library. 1936.

49. Morette, A. and Gaudefroy, G., Bull. soc. chim. France, 1951, 73.

50. Moser, L., Z. anorg. u. allgem. Chem., 105, 112 (1919).

51. Munro, L. A. and McCubbin, J. W., Trans. Roy. Soc. Canada, III(3), 28, 29 (1934).

52. N. V. de Bataafsche Petroleum Maatschappij. Dutch Patent 63,040. May 16, 1949. Abstracted in Chem. Abst. 43: 6654. 1949.

53. Pease, R. N., J. Am. Chem. Soc., 45, 1196 (1923).

54. Pease, R. N., J. Am. Chem. Soc., 45, 2296 (1923).

55. Prandtl, W. and Mursohhauser, H., Z. anorg. Chem., 56, 173 (1907).

56. Ramsey, J. B., J. Am. Chem. Soc., 49, 1138 (1927).

57. Roiter, W., Gauchmann, S. and Leperson, M., Acta Physicochim. (U. R. S. S.), 4, 145 (1936).

58. Russell, W. M. and Taylor, H. S., J. Phys. Chem., 29, 1325 (1925).

59. Scott, W. W. Standard Methods of Chemical Analysis. 5th ed. Vol. I. p. 394. New York. D. Van Nostrand Co., Inc. 1939.

60. Seidel, A. Solubilities of Inorganic and Metal Organic Compounds. 3d ed. Vol. I. New York. D. Van Nostrand Co., Inc. 1940.

61. Sevag, N. G., Smolens, J. and Lackman, D. B., J. Biol. Chem., 134, 523 (1940).

62. Shriner, R. L. and Fuson, R. C. Systematic Identification of Organic Compounds. 2d ed. p. 136. New York. John Wiley and Sons, Inc. 1940.

63. Stanerson, B. R. A Correlation between Adsorption of Hydrogen and Activity of Some Catalysts Containing Oxides of Copper. Unpublished Ph. D. Thesis. Ames, Iowa, Iowa State College Library. 1939.

64. Stewart, M. M. Some Metallic Oxides as Promoters for Copper Oxide Catalysts in the Hydrogenation of Furfural. Unpublished Ph. D. Thesis. Ames, Iowa, Iowa State College Library. 1940.

65. Taylor, H. S., J. Am. Chem. Soc., 53, 578 (1931).

66. Taylor, H. S. and Burns, R. M., J. Am. Chem. Soc., 43, 1273 (1921).

67. Taylor, H. S. and Glasstone, S. Atomistics and Thermodynamics. p. 573. New York. D. Van Nostrand Co., Inc. 1942.

68. Taylor, H. S. and Jungers, J. C., J. Am. Chem. Soc., 57, 660 (1935).

69. Taylor, H. S. and McKinney, P. V., J. Am. Chem. Soc., 53, 3604 (1931).

70. Taylor, H. S. and Ogden, G., Trans. Faraday Soc., 30, 1178 (1934).

71. Turkevich, J. and Taylor, H. S., J. Am. Chem. Soc., 56, 2254 (1934).

72. Twigg, G. H., Proc. Roy. Soc. (London), 188A, 92 (1946).

73. Twigg, G. H., Discussions Faraday Soc., 1950, No. 8, 152.

74. Twigg, G. H. and Rideal, E. K., Trans. Faraday Soc., 36, 533 (1940).

75. Ubaldini, I. and Guerrieri, F., Ann. chim. applicata, 38, 695 (1948).

76. Willard, H. H. and Diehl, H. Advanced Quantitative Analysis. 1st ed. p. 247. New York. D. Van Nostrand Co., Inc. 1943.

77. Willard, H. H. and Furman, N. H. Elementary Quantitative Analysis. 3d ed. p. 444. New York. D. Van Nostrand Co., Inc. 1940.

78. Willard, H. H. and Thompson, J. J., Ind. Eng. Chem., Anal. Ed., 3, 398 (1931).